W71-06250

WATER POLLUTION CONTROL RESEARCH SERIES

PB 198 225

Treatment of Acid Mine Drainage by Ozone Oxidation

Reproduced by
NATIONAL TECHNICAL
INFORMATION SERVICE
Springfield, Va. 22151

WATER POLLUTION CONTROL RESEARCH SERIES

The Water Pollution Control Research reports describe the results and progress in the control and abatement of pollution in our Nation's waters. They provide a central source of information on the research, development, and demonstration activities in the Environmental Protection Agency, Water Quality Office, through inhouse research and grants and contracts with Federal, State, and local agencies, research institutions, and industrial organizations.

A [illegible] card sheet is included in the report to facilitate information retrieval. Space is provided on the card for the user's accession number and for additional uses.

Copies of reports previously issued in the Water Pollution Control Research Series can be obtained as indicated on the Publication Notice page. Reports not included in the series, and those published after this report, may be obtained from the Water Quality Office, Washington, D. C.

1 Accession Number	2 Subject Field & Group	SELECTED WATER RESOURCES ABSTRACTS INPUT TRANSACTION FORM
WRI-76250	04D	

5 Organization

Brookhaven National Laboratory
Upton, New York ~~11973~~

6 Title

Treatment of Acid Mine Drainage by Ozone Oxidation,

10 Author(s)

M.Beller
C.Waide
M.Steinberg

16 Project Designation ~~EPA-WQO Grant 14010 FMH~~
EPA-WQO Contract No. 14-12-838

21 Note

Copy available from GPO Sup Doc as , $1.00 ; microfiche from NTIS as PB 198 225, $0.95.

22 Citation

Environmental Protection Agency-WQO Report 14010FMH, ~~12/70~~ Dec, 1970, 91p, 23 fig, 28 tab, 40 ref

~~Washington, D.C. 20242~~

23 Descriptors (Starred First)

*Mine Drainage, neutralization, ~~ferric iron~~
*Iron Oxidation, limestones, treatment, ~~costs~~
*Ozone, ~~ferrous~~ iron, Waste water treatment,
Industrial wastes, Costs, Oxidation,

25 Identifiers (Starred First)

Ferrous iron, Ferric iron

27 Abstract An engineering design and economic study to evaluate the feasibility of ozone oxidation and limestone neutralization of Acid Mine Drainage (AMD) was performed. The study concludes that an ozone process is feasibile, compares economically with existing processes, and offers potential advantages in process control, reduced neutralization costs, and simplified AMD sludge handling and disposal. Ozone production by electric discharge and radiation processes are compared both for on-site and central plant installations utilizing ozone shipping and storage facilities. A central chemonuclear ozone production plant with a distribution system is found to be most economical, followed by electric discharge central and onsite plants. Design and construction of a mobile pilot plant which employs electric discharge ozonizers is recommended for field trials of the process.

This report was prepared in fulfillment of Contract No. 14-12-838 between the Federal Water Quality Administration and Brookhaven National Laboratory.

Key words: Mine drainage, ozone treatment, treatment costs, neutralization, limestone, oxidation, ferrous iron, ferric iron.

Abstractor M. Steinberg

Institution Brookhaven National Laboratory

WR:102 (REV JULY 1969)
WRSIC

SEND TO: WATER RESOURCES SCIENTIFIC INFORMATION CENTER
U.S. DEPARTMENT OF THE INTERIOR
WASHINGTON, D. C. 20240

* GPO: 1969-359-339

Treatment of Acid Mine Drainage by Ozone Oxidation

Department of Applied Science
Brookhaven National Laboratory, Associated Universities, Inc.
U.S. Atomic Energy Commission
Upton, New York 11973

for the

ENVIRONMENTAL PROTECTION AGENCY

Contract No. 14-12-838
Project No. 14010 FMH

December 1970

For sale by the Superintendent of Documents, U.S. Government Printing Office
Washington, D.C., 20402 - Price $1

EPA Review Notice

This report has been reviewed by the Environmental Protection Agency and approved for publication. Approval does not signify that the contents necessarily reflect the views and policies of the Environmental Protection Agency, nor does mention of trade names or commercial products constitute endorsement or recommendation for use.

ABSTRACT

An engineering design and economic study to evaluate the feasibility of ozone oxidation and limestone neutralization of Acid Mine Drainage (AMD) was performed. The study concludes that an ozone process is feasible, compares economically with existing processes, and offers potential advantages in process control, reduced neutralization costs, and simplified AMD sludge handling and disposal. Ozone production by electric discharge and radiation processes are compared both for on-site and central plant installations utilizing ozone shipping and storage facilities. A central chemonuclear ozone production plant with a distribution system is found to be most economical, followed by electric discharge central and on-site plants. Design and construction of a mobile pilot plant which employs electric discharge ozonizers is recommended for field trials of the process.

This report was prepared in fulfillment of Contract No. 14-12-838 between the Federal Water Quality Administration and Brookhaven National Laboratory.

Key Words: Mine drainage, ozone treatment, treatment costs, neutralization, limestone, oxidation, ferrous iron, ferric iron.

CONTENTS

		Page
	Abstract	
	List of Figures	
	List of Tables	
1.	Introduction	1
2.	Summary and Conclusions	5
3.	Recommendations	7
4.	AMD Treatment Process Design	9
5.	Ozone Production Methods	17
	5.1 General Considerations	17
	5.2 Electric Discharge Synthesis	19
	5.3 Radiation and Chemonuclear Synthesis	20
	5.4 New Methods	24
	5.5 Process Descriptions	25
	5.5.1 Isotopic Process	25
	5.5.2 Electric Discharge Process	25
	5.5.3 Chemonuclear Process	25
6.	Economic Analysis	31
	6.1 On-Site Plants	31
	6.1.1 Isotopic Process	31
	6.1.2 Electric Discharge Process	41
	6.2 Central Ozone Production Plants	49
	6.2.1 Ozone Shipping and Storage	49
	6.2.2 Chemonuclear Process and Comparison with Electric Discharge Process	52
	6.3 AMD Treatment Plant	65
	6.4 Comparison with Present Methods	79

CONTENTS (Cont'd)

		Page
7.	Discussion	81
	Acknowledgement	83
	References	84
	Appendix	A-1

LIST OF FIGURES

No.		Page
1	AMD Oxidation and Neutralization Process System	12
2	Brookhaven Chemonuclear In-pile Research Loop	22
3	History of Run No. 3	23
4	Ozone Generation Using Isotopic Sources	26
5	Electric Discharge Ozone Process for Water Treatment	27
6	Chemonuclear Ozone Generation and Purification for Water Treatment	28
7	Gamma-ray Energy Absorption in O_2 vs Path Length	33
8	Ozone Yield vs Oxygen Pressure	34
9	Investment Cost for Ozone Using Isotopic Radiation	36
10	Cesium-137 Ozone Generator, Production Cost vs Capacity	37
11	Cobalt-60 Ozone Generator, Production Cost vs Capacity	38
12	Isotopic Source Ozonizers, Cost of AMD Ozonation at Varying Stream Flows	39
13	Electric Discharge Ozonizers, Production Cost vs Capacity	45
14	Electric Discharge Ozonizers, Cost of AMD Ozonation-Once-Through Air Feed	46
15	Electric Discharge Ozonizers, Cost of AMD Ozonation-Oxygen Feed and Recycle	47
16	Ozone Storage and Distribution System	50
17	Distribution of Draining Coal Mines in Pennsylvania Counties	51
18	Production Cost of Ozone, Conventional vs Chemonuclear Processes	53
19	Electric Discharge vs Chemonuclear AMD Treatment Plant Costs Using Ozone, Large Central Plants	54
20	Total AMD Treatment Cost Using Ozone-Electric Discharge Ozonizers-On-site Generation	71
21	Total AMD Treatment Cost Using Electric Discharge Ozone-Central Plant Ozone Generation, Shipped to AMD Site	72

LIST OF FIGURES, cont'd.

No.		Page
22	Total AMD Treatment Cost Using Chemonuclear Ozone, Central Plant Ozone Generation, Shipped to AMD Site	73
23	Total Plant Investment for AMD Treatment Using On-site Electric Discharge Ozone	75

LIST OF TABLES

No.		Page
1	Typical AMD Stream Compositions	10
2	AMD Plant Material Balance	13
3	Ozone Requirements for AMD Streams	15
4	Energy Requirements for Ozone Synthesis	18
5	Characteristics of BNL Gamma Sources	32
6	Ozone Investment Costs, On-site Generation, Once-Through Air Feed	42
7	Ozone Production Costs, On-site Generation, Once-Through Air Feed	42
8	Ozone Investment Costs, On-site Generation, Recycled Oxygen Feed	43
9	Ozone Production Costs, On-site Generation, Recycled Oxygen Feed	43
10	Cost of Purchased Oxygen Gas	44
11	Chemonuclear Ozone - Total Production Cost	55
12	Chemonuclear Ozone - Investment Cost	56
13	Electric Discharge Production Cost	57
14	Electric Discharge Ozone Investment Cost	57
15	Chemonuclear Ozone System Power Requirements	58
16	Electric Discharge Ozone System Power Requirements	59
17	Chemonuclear Ozone Energy Requirements	59
18	Electric Discharge Ozone Energy Requirements	60
19	Storage and Distribution System	63
20	AMD Plant Cost	66
21	AMD Treatment Plant Operating Cost	67
22	AMD Treatment Total Operating Cost, Ozone Generated On-site, Electric Discharge	68
23	Ozone Generated in 40 Ton/Day Central Plants	69
24	Ozone Generated in 200 Ton/Day Central Plants	70
25	Total Investment Costs for AMD Treatment Using On-site Ozone with Recycled Oxygen Feed	74
26	Comparison of AMD Total Treatment Costs	76
27	Cost Breakdown for Total AMD Treatment of Pennsylvania AMD Streams	78
28	Cost of Conventional AMD Treatment	80

1. INTRODUCTION

The problem created by acid mine drainage (AMD) has been reported in great detail in recent years.[1,2] The formation of "yellowboy" in streams and the effect of mine drainage on water quality in mining areas has prompted a considerable research and development effort in regard to the treatment of acid mine drainage.

Treatment studies have, in general, considered the neutralization of the mine drainage using various low cost materials such as limestone,[39,40] lime and sodium carbonate, followed by or concurrent with an aeration step to oxidize iron from the ferrous to the ferric state. The resultant precipitate of iron and various neutralization products are then separated and removed from the bulk flow of treated water.

The work being done in the development of water treatment techniques has served to point up the wide range of problems associated with AMD treatment.[3,4] Air oxidation is a relatively slow process, dependent on the pH of the water and the rate of aeration. Precipitate quality can be quite poor depending on several factors including the type of neutralizer used, whether sludge recycling is practicable, and the point at which process oxidation occurs. High alkalinity is required to get the most favorable reaction rates but excessive neutralizer use adds to the sludge handling problems and presents a risk of discharging highly alkaline waters to streams. In general, the wide variability in AMD composition has led to a number of treatment methods which are adequate for specific mine and mine water conditions but which may not be capable of being applied elsewhere without some degree of modification.

In this study, ozone is evaluated as an oxidizing agent for the oxidation of the iron in AMD from the ferrous to the ferric state.

The scope of the study includes a detailed engineering design and cost estimate for the production and supply of ozone, and evaluation of the entire AMD oxidation-neutralization treatment process. The ozone production and distribution processes investigated are as follows:

1. The synthesis of ozone by isotopic radiation using ^{60}Co and ^{137}Cs gamma radiation sources.

2. The synthesis of ozone by the corona electric discharge process.

3. The synthesis of ozone by the chemonuclear reactor process.

4. The problems of shipping ozone from a central production plant are examined, and shipping costs to mine drainage sites are estimated.

The use of ozone for AMD treatment has been investigated by Rozelle, et al[6] and a number of favorable conclusions regarding its application can be drawn from that work.

A comparison of the use of oxygen and ozone for oxidation of Fe^{+2} to Fe^{+3} is made by Rozelle through the use of the following equations. The sequence for the reaction with oxygen in aqueous solution[6,38] is as follows:

(1) Hydrolysis

$$Fe^{+2} + 2H_2O \rightleftharpoons Fe(OH)_2 + 2H^+$$

(2) Neutralization

$$2H^+ + 2OH^- \rightleftharpoons 2H_2O$$

(3) Oxidation of Fe^{+3}

$$2Fe^{+2} + \tfrac{1}{2}O_2 + 4OH^- + H_2O \rightarrow 2Fe(OH)_3$$

Hydrolysis curves for the complete neutralization of the combined acid in the ferrous iron system show that sufficient alkaline reagent must be added to bring the pH to a value of 10.[6]

On the other hand, using ozone for oxidation in low pH solutions, the following system of equations is presented.

(1) Oxidation

$$2Fe^{+2} + O_3 + 2H^+ \rightleftharpoons 2Fe^{+3} + H_2O + O_2$$

(2) Hydrolysis

$$Fe^{+3} + 3H_2O \rightleftharpoons Fe(OH)_3 + 3H^+$$

(3) Neutralization

$$3H^+ + 3OH^- \rightleftharpoons 3H_2O$$

The hydrolysis reaction involves a number of immediate species and their formation is described by Rozelle, et al as being similar to the following:

(1) $Fe^{+3} + H_2O \rightleftharpoons Fe(OH)^{+2} + H^+$

(2) $2Fe^{+3} + 2H_2O \rightleftharpoons Fe_2(OH)_2^{+4} + 2H^+$

(3) $Fe(OH)^{+2} + H_2O \rightleftharpoons Fe(OH)_2^{+} + H^+$

(4) $Fe(OH)_2^{+} + H_2O \rightleftharpoons Fe(OH)_3 + H^+$

The net combined acid released in the oxidation and hydrolysis is the same for either oxygen or ozone treatment. Neutralization of the combined acid associated with oxidation of Fe^{+2} by ozone can be accomplished at pH values of approximately 3.[6] However, hydrolysis takes place at a rapid rate at a pH of 4 or above. Consequently, neutralizer quantities are expected to be lower since only enough neutralizing agent need be added, beyond that required to handle the combined acid, to bring the water to a pH where precipitate quality and rate of coagulation is best. This value is in the pH 5-7 range.[5]

Increased reaction rates and better precipitate quality will minimize holdup times and the need for solids-liquid separating equipment. Precipitation of Fe^{+3} below the isoelectric point ($pH \simeq 7$) results in a dense precipitate of 15-20% solids,[6] while precipitation of Fe^{+2} above this point yields a voluminous flocculant precipitate. The effectiveness of ozone as an oxidizing agent is also expected to extend to removal of other metal ions such as Mn^{+2} and Al^{+3} in the acid mine drainage waters.

Steinberg, et al, in a series of papers,[11] discussed the utilization of high energy radiation in treating acid mine drainage. This work included a study of the use of radiation in conjunction with neutralization using mechanically agitated limestone. The conclusions reached in this study point out the effectiveness of the limestone treatment in terms of the rate of removal of iron and precipitate quality. The use of lime in conjunction with limestone as adopted by some investigators[1] would seem to be unnecessary and undesirable when viewed in the context of the work of Rozelle and Steinberg. Using ozone to first oxidize the ferrous iron would allow precipitation and removal of iron to occur at low pH values. Thus, the buffering action of CO_2 resulting from the use of limestone would not be a limiting factor in the process and would, in fact, eliminate the possibility of over-neutralization and the need for fine control which the use of lime entails.

2. SUMMARY AND CONCLUSIONS

The economics of using ozone for treatment of Acid Mine Drainage (AMD) are evaluated. The treatment consists of rapid oxidation of ferrous to ferric iron with ozone and neutralization with limestone. Ozone production is considered using electrical discharge, isotopic radiation and chemonuclear methods. Ozone production facilities are evaluated both at the usage point and for large central plants in conjunction with a distribution system. Designs for these systems are outlined, and appear feasible. The ranges used in the study are AMD flows from 250,000 to 6,000,000 gal. per day containing Fe^{+2} concentrations varying from 50 to 1,000 ppm.

In general, both chemonuclear and electric discharge central ozone production plants with a distribution system offer clear economic advantages over on-site plants except for AMD streams with low Fe^{++} content (~50 ppm) and low flows (250,000 gpd). The treatment costs vary with Fe^{+2} content and AMD flow. These costs are estimated to range from 9-13¢ per 1,000 gal. AMD treated at 50 ppm Fe^{+2} over the entire flow regime studied. At 300 ppm Fe^{+2}, the treatment costs are 18-34¢ per 1,000 gal., and at 1,000 ppm the cost range increases to 40-78¢ per 1000 gal.

The lowest cost in each of the above ranges applies to central plants with distribution systems, high AMD flow rates, and ozone production via the chemonuclear process. The highest cost in each range is for on-site electric discharge ozone at low flow rates.

The isotopic radiation process is less economical but might be useful for very low flow and low Fe^{+2} content streams.

Ozone oxidation with limestone neutralization competes favorably with the presently used air oxidation and lime neutralization system on an economic basis. Conventional methods have been estimated to range from $0.10-$1.30 per 1000 gal.; the present study estimates

that the ozone-limestone process ranges from $0.09-$0.78. An estimate for a specific case of 1,000,000 gpd and Fe^{+2} concentration of 150 ppm results in a treatment cost of $0.17 per 1000 gal. using the air-lime method. The ozone-limestone process can treat the same stream for $0.13-$0.16. The investment cost is $350,000 for the conventional air-oxidation and lime process, compared with an estimate of $280,000 for an on-site electric discharge ozone-limestone facility. The investment cost using ozone from a central plant, and including on-site ozone storage equipment, would be $184,000.

The investment cost necessary to treat the entire AMD of southwestern Pennsylvania, estimated at 486,000,000 gal. per day, would be $182,000,000, based on the use of a 200-ton per day central chemonuclear ozone plant. The investment cost includes ozone storage and shipment facilities and AMD treatment equipment at each of the approximately 2160 sites in the region. Each site is assumed capable of handling an average flow of 250,000 gal. per day. A central electric discharge plant would require an investment of about $191,000,000. Since the chemonuclear system requires additional development, the initial plant cost for both chemonuclear and electric discharge ozone are roughly comparable; however, the chemonuclear plant operating costs are lower.

The study concludes that the ozone-limestone system offers the potential of simplified process control, higher plant throughput, removal of additional pollutants from AMD, and reduced sludge-handling requirements at costs equal to or less than those obtained using present techniques.

3. RECOMMENDATIONS

It is recommended that a mobile pilot plant be built which incorporates an electric discharge ozonizer system for trials at AMD sites which have varying Fe^{+2} contents and flows. This will permit evaluation of the ozone-limestone system under actual field conditions, and will also provide data for large-scale design of treatment plants. The chemonuclear system has economic advantages in the long-term picture, but will require additional expenditures associated with its development. Since the electric discharge system is presently available and appears economic, it is recommended that present emphasis be placed on development of AMD cleanup using the electric discharge method for ozone supply and on-site plants. New methods of ozone production, which may offer even greater economic advantages, should also be explored.

It is also recommended that, because of the economic incentives offered by central ozone generating plants with distribution systems, effort should be expended in the area of ozone storage and shipment technology.

BLANK PAGE

4. AMD TREATMENT PROCESS DESIGN

Because acid mine waters range widely in flowrate and composition, three flows and ferrous iron compositions were selected which generally encompass the conditions existing at typical AMD sites. The AMD flow rates chosen are 6,000,000, 1,000,000, and 250,000 gallons per day, containing ferrous iron contents of 1000, 300, and 50 parts per million. Apart from the ozone treatment vessel, the remaining plant components are based on those used or tested in various AMD treatment plants or plant studies. A basic plant design was considered here for two reasons. First and most significant is the belief that oxidation of Fe^{+2} to Fe^{+3} with ozone at low pH values will improve later neutralization and precipitation steps to an extent not experienced in other studies. The second consideration is the recognition that the variety of mine waters and sources that are encountered make it impractical to cover each case. By presenting a plant design which is applicable to a widely varying flow and composition regime, any additional complications brought about by use in a specific location can be factored in by the designer with a minimum of difficulty. The neutralization process detailed here was based on neutralization of the acidity generated in the oxidation and hydrolysis reactions with an AMD having an initial pH of 2.5.

The acidity resulting from the oxidation and hydrolysis reactions is referred to as "combined acid." The acidity associated with the initial pH of the water is considered to be "free acid." Total acidity is the sum of the combined and free acid values. In all cases, these have been described in terms of the quantity of $CaCO_3$ necessary to react with the acid present.

Ranges and average values for some typical AMD stream compositions are shown in Table 1.

PRECEDING PAGE BLANK

TABLE 1

TYPICAL AND STREAM COMPOSITIONS

All values in mg/l

	Range*	Average*
pH	2.5-3.2	3.1
Total acid (as $CaCO_3$)	86-4080	1130
Total Fe	1.3-815	280
SO_4	290-10,000	3080
Mn	4.4-38	16
Ca	4-440	220
Mg	0-404	154
Al	24-900	223

*Based on 5 AMD Sites[37]

The values of Fe^{+2} and total acidity used for the study are summarized below. For simplicity, any acid resulting from the hydrolysis of metal ions other than iron has been ignored.

Fe^{+2} conc.-ppm	pH	Total Acid (mg/l $CaCO_3$)
1000	2.5	1900
300	2.5	650
50	2.5	200

The AMD treatment plant is designed to meet the Pennsylvania legal requirements for discharge of 7 ppm maximum iron, and pH between 6 and 9. Ozone treatment and limestone neutralization can permit treated water to be discharged at pH 6-7, meeting state water quality standards. Laboratory tests indicate that the iron content can be reduced to less than 1 ppm.[6]

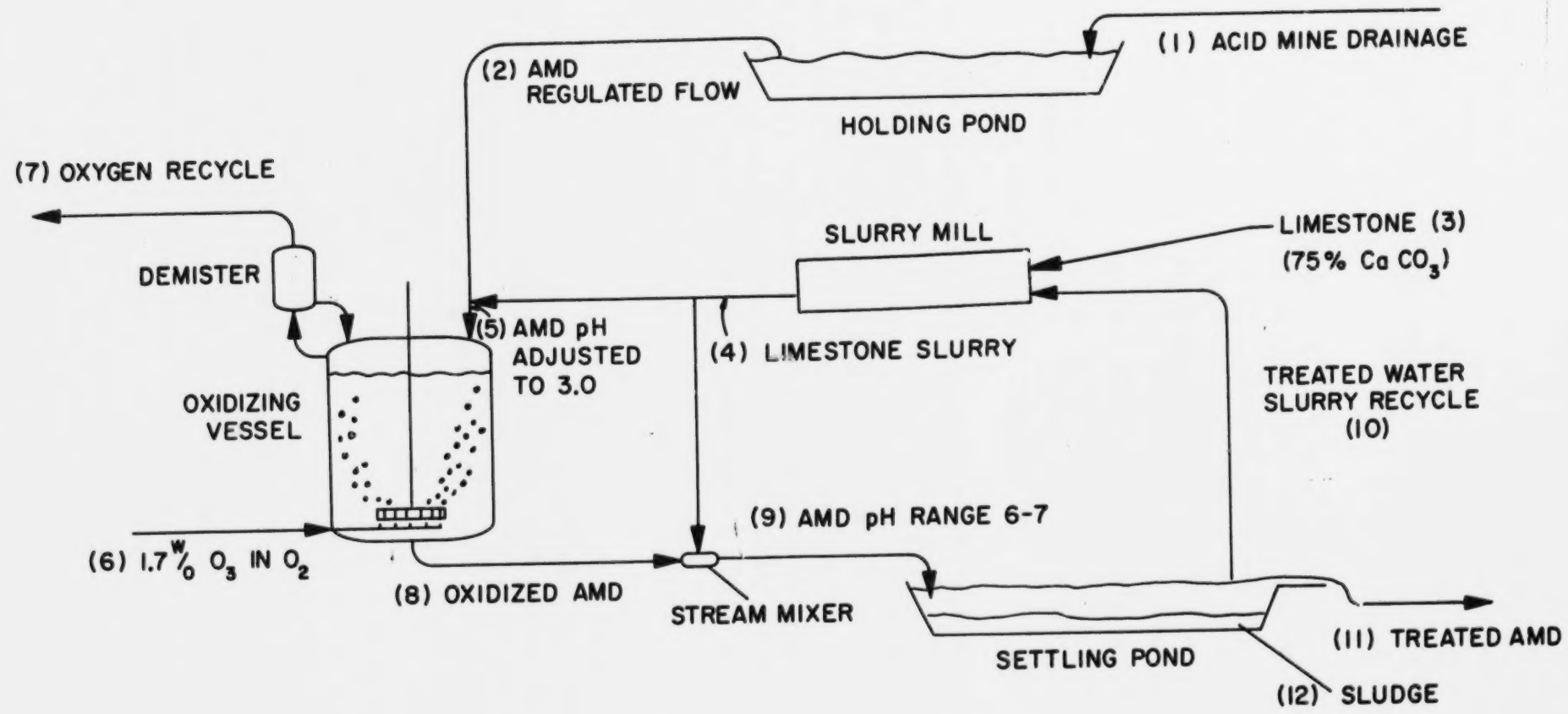
The ozone process treatment plant and ozone treatment methods are described in the following sections. Fig. 1 is a schematic of the process and Table 2 is a material balance for all corresponding AMD stream conditions of iron content and flow rate.

The three nominal flow rates and ferrous iron concentrations used to size the treatment plant have been described. It is assumed as well that the flow of mine drainage will vary to some extent through the day. Recognizing the desirability of a constant plant throughput, a holding pond with a controlled outlet flow rate has been provided at the head end of the plant. For plants with a low flow rate, the holding pond could be used for storage of water during the night shift, thereby reducing plant operation to a one or two shift basis.

This process permits the use of limestone for neutralization, since all the iron is in the ferric state after ozone treatment and precipitation will occur at pH 5-7. Limestone is cheap, readily available and, in conjunction with an ozone process, is an effective neutralizer. A limestone slurry is produced by loading a tumbling mill with bulk limestone and providing a flow of water to give the slurry mix desired. A slurry with particle sizes less than 400 mesh is produced. Otherwise a slurry can be produced by mixing limestone powder and water in a mixing tank. Over-all costs would not be significantly different and the method chosen would depend on local preference. For this study, limestone containing 75% $CaCO_3$ was used as a basis for sizing equipment. Based on this $CaCO_3$ content, a limestone quantity in slight excess of the stoichiometric amount was chosen as a reference point for this study.

Ozone is produced as a 1.7 weight per cent mixture (1% by volume) in a gaseous oxygen stream. It is supplied to the oxidizing contactor, and after reacting with the AMD, is recycled to the ozone production unit.

AMD from the holding pond is fed to the oxidation vessel after an initial pH adjustment with limestone slurry. The pH adjustment is included, subject to experimental verification, on the basis of information



AMD OXIDATION & NEUTRALIZATION PROCESS SYSTEM

FIGURE 1

TABLE 2

AMD PLANT MATERIAL BALANCE

T/d = tons per day

Case	(1) AMD gpd	(2) Fe^{++} ppm / T/d	(3) $CaSO_4$ T/d	(4) Slurry gpd	(5) Adj AMD gpd	(6) O_3+O_2 T/d	(7) O_2 Recycle T/d	(8) Oxid. AMD gpd	(9) Neutral AMD gpd	(10) water recycle gpd	(11) Treated AMD flow gpd	(11) Sol $CaSO_4$ T/d	(12) Sludge $CaSO_4$ T/d	(12) $Fe(OH)_3$ T/d	(12) Misc. T/d	(13) O_3 Loss with (8) T/d	(14) O_3 in (6) T/d	(15) O_2 in (6) T/d	(16) O_2 loss T/d
1	$6x10^6$	1000/25	63	$13x10^5$	$6.1x10^6$	736	730	$6.1x10^6$		$1.3x10^5$	$6x10^6$	50	13	48	16	0.18	125	723	1.25
2	"	300/7.5	21	$45x10^4$	$6x10^6$	224	221	$6x10^6$		$4.5x10^4$	"	21	-	14.4	5	0.18	3.8	220	1.25
3	"	50/1.3	6	$14x10^4$	"	36	35	$6x10^6$		$1.4x10^4$	"	6	-	2.4	1.5	0.18	0.6	35	1.25
4	$1x10^6$	1000/4	10	$18x10^4$	$1x10^6$	123	122	$1x10^6$		$1.8x10^6$	$1x10^6$	9	1	7.9	2.6	0.03	2.1	121	0.21
5	"	300/1.2	3.5	6200	"	36	35	$1x10^6$		6200	"	3.6	-	2.4	0.9	0.03	0.6	35	0.21
6	"	50/0.2	1.0	2230	"	6	6	$1x10^6$		2230	"	1.0	-	0.4	0.1	0.03	0.1	6	0.21
7	$\frac{1}{2}x10^6$	1000/1	2.5	5200	$\frac{1}{2} \times 10^6$	30	29	$\frac{1}{2}x10^6$		5200	$\frac{1}{2}x10^6$	2	0.5	1.9	0.5	0.007	0.5	29	0.05
8	"	300/0.3	0.9	1740	"	9	9	$\frac{1}{2}x10^6$		1740	"	0.9	-	0.6	0.2	0.007	0.15	9	0.05
9	"	50/0.05	0.25	500	"	2	2	$\frac{1}{2}x10^6$		500	"	0.3	-	0.1	0.1	0.007	0.03	2	0.05

suggesting that the oxidation might be enhanced by operation with the pH at or slightly above a value of 3. It is known that hydrolysis of Fe^{+3} occurs above a pH of 3 and that some cations, possibly those present in limestone, have a catalytic effect on the oxidation process.[5] In addition, Rozelle, et al[6] found sulfate in measureable amounts in precipitates formed in low pH (<2.7) solutions but only traces of sulfate in precipitates from solutions of pH 3.5. The pH adjustment to pH 3.5 thus would also prevent premature sulfate precipitation in the oxidation vessels.

A turbine type mixer has been used in the oxidizing vessel for purposes of this study. This type of contacting device should be more than sufficient for the AMD-ozone system and provides a conservative design in terms of equipment and power costs. Actually, values for contacting efficiency were chosen using Roselle's data.[6] These were based upon studies using simple bubbler type contacting devices in which contact times and areas were small. Again, the data provides conservative values for use in this study. The specific nature of previous work in gas-liquid contacting studies makes a more rigorous application and scale-up of the data to the AMD-ozone system difficult. Experimental work to verify the applicability of available correlations is necessary.[8, 9, 10]

Following oxidation of the ferrous iron, limestone slurry is added to the stream from the oxidizing vessel, and turbulence is used to provide mixing. In the absence of ferrous ion, precipitation should be relatively rapid and in a form favorable to rapid settling in the final settling pond. Results of neutralization tests with limestone slurry indicate that neutralization should be substantially complete by the time the material reaches the settling pond.[7]

Ozone requirements for the various cases on which the study is based are shown in Table 3.

TABLE 3

OZONE REQUIREMENTS FOR AMD STREAMS

LB/DAY OZONE

Fe^{++} Conc.-ppm	AMD Stream Flow-Gal./Day 0.25×10^6	1.0×10^6	6.0×10^6
50	52	208	1,248
300	312	1,248	7,488
1,000	1,040	4,160	24,960

The ozone requirements are based on the stoichiometry of the oxidation reaction:

$$2Fe^{+2} + O_3 + 2H^+ \rightleftharpoons 2Fe^{+3} + H_2O + O_2$$

One mole of ozone oxidizes 2 moles of Fe^{+2}. On a mass basis, 0.43 lb of ozone oxidizes 1 lb of Fe^{+2}. At the 86% utilization efficiency which Rozelle[6] obtained in his work, the ozone uptake for oxidation becomes:

$$0.5 \text{ lb } O_3/\text{lb } Fe^{+2}$$

This can also be expressed as:

$$0.417 \text{ lb } O_3/100 \text{ ppm } Fe^{+2}/1000 \text{ gal./day AMD}$$

BLANK PAGE

5. OZONE PRODUCTION METHODS

5.1 General Considerations

Ozone is produced by the introduction of energy into an oxygen-containing stream. The formation reaction is endothermic. The ozone formed can also undergo thermal decomposition, thus accounting for the relatively low efficiency and the large energy requirement for its production. High energy (~5eV) is required to break the oxygen bond to form an O atom, which then combines with an O_2 molecule to yield an O_3 molecule. The energy necessary can be obtained by photochemical radiation, nuclear radiation, or electrical discharge. The over-all reaction is:

$$3/2\ O_2\ (g) \rightarrow O_3(g)$$

and the enthalpy of reaction is:

$$\Delta H_{298.2} = 34\ \text{Kcal/mole}$$

The minimum thermodynamic energy requirement is thus 34 Kcal of energy to form a mole of ozone. As a comparison, one can consider the practical present-day achievable efficiencies, shown in Table 4. Electrical discharge ozonizers operating with oxygen have energy requirements ranging from 3.75 to 5.0 kw-hr./lb ozone, which is equivalent to a G-value of 6.8 to 5.1. G-values ranging from 10-15 can be achieved using high energy radiation, offering a potential doubling in the efficiency of ozone production. G-value is a measure of chemical production for a given energy input, and is defined as the number of molecules of product resulting from the input of 100 eV of energy into the reactant.

Table 4 shows that the more efficient methods are isotopic sources, which generate gamma radiation, chemonuclear fission fragment sources, and electric discharge ozonizers. These three methods were chose for economic evaluation.

PRECEDING PAGE BLANK

TABLE 4

ENERGY REQUIREMENTS FOR OZONE SYNTHESIS

Method	Energy Yield - Kw. Hr/lb Ozone		% Over-all Thermal Efficiency
	Electrical	Thermal Energy Equivalent	
Electric Discharge in Oxygen	3.75	11.2[1]	3.3
Electric Discharge in Air	7.25	21.8[1]	1.7
Chemonuclear (Fission Fragment)	--	4.8[2]	7.7
Isotopic Sources (Gamma)	--	3.4[3]	10.9
Photochemical	18.0	54.0[1]	0.7
Theoretical Thermodynamic	--	0.37	100.0

1) 33% Power Conversion Efficiency, Thermal to Electrical

2) 35% Energy Deposition Efficiency

3) 50% Energy Deposition Efficiency

PRECEDING PAGE BLANK

5.2 Electric Discharge Synthesis

Ozone is presently produced almost entirely by the electric discharge process. The apparatus[31] designed to produce ozone by this method is called an ozonizer, and consists of a pair of electrodes separated by glass insulators and an air space. When a high voltage (50,000 v) alternating current is applied, the air space is filled with a diffused glow (a corona discharge). The insulators prevent sparking or arcing, and the alternating current provides polarity reversal, permitting accumulation and discharge of electrons during each half cycle. When air or oxygen is passed through the air space, the electron release provides the energy necessary to produce ozone. Since more than 90% of the applied energy is dissipated as heat, cooling must be provided for the electrodes and the ozone must be removed rapidly to prevent thermal decomposition.

For a given energy input, twice as much ozone can be generated from an oxygen stream as from an air feed. The oxygen must be recycled since it contains only 1% by volume of ozone, and it is not economic to discard it. Therefore, recycling pumps and driers are necessary for an oxygen feed system.

The electric discharge method has resulted in rather limited usage of ozone, since power consumption and investment costs are high, and the advantages of large scale are difficult to achieve for two reasons. First, because electric discharge units are, at best, rather small capacity individual devices, a large multiplicity of the machines is required. Second is the problem of ozone shipment. Ozone is presently shipped[12] in small quantities; however, there seems to be no technical reason to prevent the implementation of the technology to large-scale shipments. It appears that the incentive to do so is lacking, possibly because the economics of large shipments has not been studied. For these reasons, ozone production economics in this report were looked at from two points of view: first, production of ozone at the usage point, with production quantities matched to the requirement of the site, and second, ozone generation at a large central facility with subsequent shipments to usage points.

5.3 Radiation and Chemonuclear Synthesis

The radiation chemistry of ozone has been studied since the early work of Lind.[13] The experiments have been mainly performed in static systems, at low pressures and at low temperatures. In liquid oxygen under static conditions in glass apparatus, an initial G value for ozone formation of 6 and high concentrations up to 6% by weight is reported by Wall and Brown.[14] In gaseous oxygen in a static steel system at a temperature of -78°C, a $G(O_3)$ value of 9 is reported by Kircher.[15] At -78°C in a static glass system at 1 atm Johnson and Warman report an initial $G(O_3)$ value of 12.8[16] In experiments by Sears and Sutherland in glass capsules in the gas phase at 1 atm O_2 in a Co^{60} field, initial $G(O_3)$ values up to 10.5 were found.[28] In capsule experiments with fission fragments in an in-pile experiment, at a temperature between R.T. and -78°C, a minimum $G(O_3)$ value of 6.9 was measured and a concentration up to 0.5% was obtained.[17] In flow systems, investigations have been made with air at room temperature and 1 atm pressure mainly for purposes of investigating the hazards of ozone formation associated with radiation processes for sterilization of medical supplies and food preservation.[18,19] In a closed glass system an O_3 concentration up to 18.5 ppm was measured and a $G(O_3)$ value up to 4.0 can be estimated from the work by Kertesz and Parsons.[18] A study by Shah and Maxie[20] in a flowing air system, constructed of glass at atmospheric pressure using gamma radiation indicated a $G(O_3)$ value of 11 at O_3 concentrations of 1.7 ppm. Flow experiments in a high pressure steel system in a Co^{60} gamma field at 68 atm and above with air at room temperature indicated a $G(O_3)$ of 4.7.[21] Recent experiments with oxygen at pressures up to 200 atm and -60°C in a stainless steel system in a radiation field gave a G value of 10.5.[22]

A G value of 13.8 was determined in pulse radiolysis experiments[23] with high energy electrons in oxygen at 1 atm and high dose rates.

For purposes of studying fission fragment chemistry in a flow system and in addition fuel behavior and product contamination problems, an in-pile research

loop was constructed and installed in the Brookhaven Graphite Reactor and was tested with pile neutron and gamma background radiation. The loop is essentially a highly versatile pilot plant.

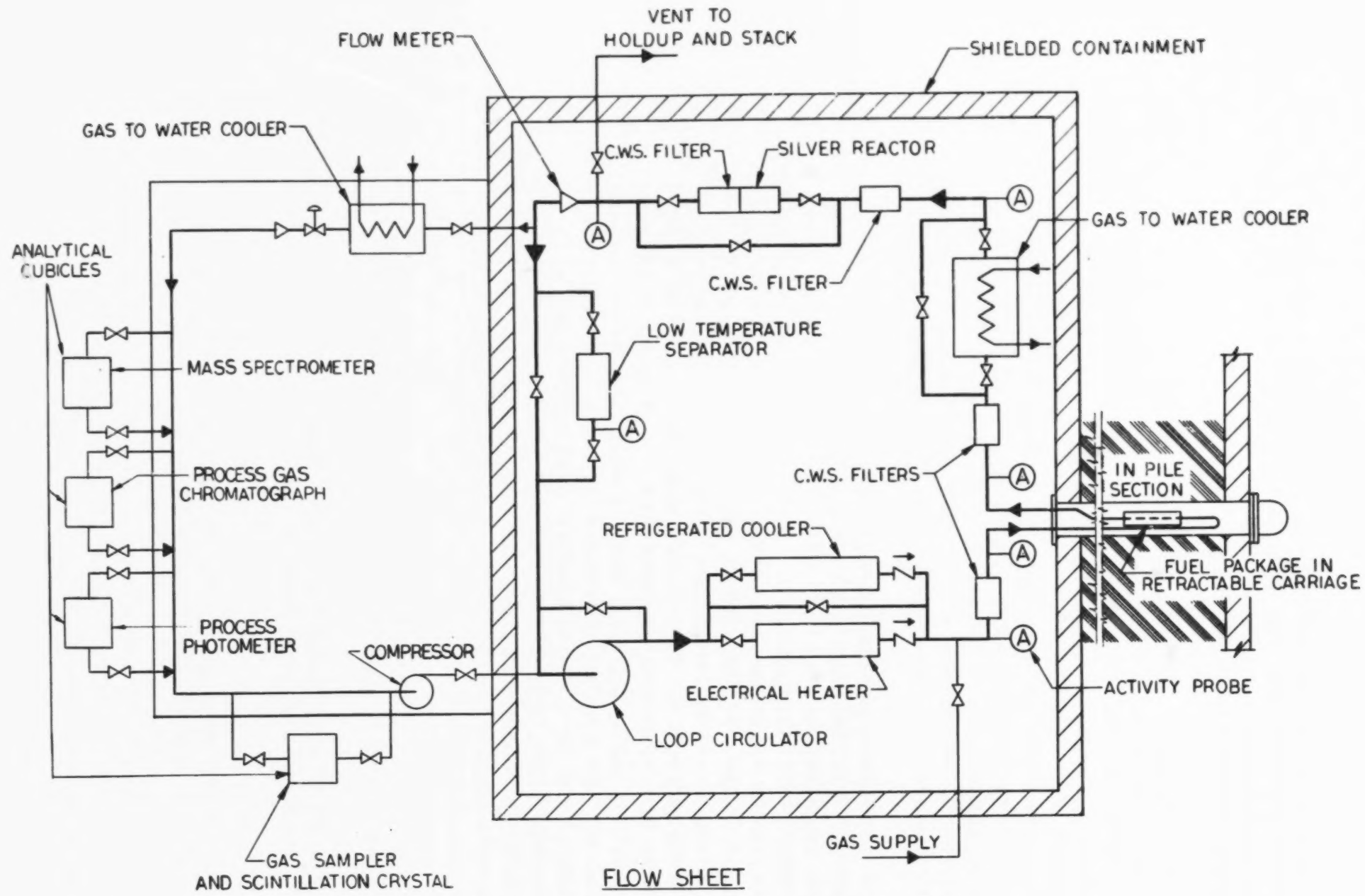
The chemonuclear loop[24] basically consists of a doubly contained, recirculating gas system which has been inserted into the lower section of the core of the Brookhaven Graphite Research Reactor. All control functions are maintained in extended out-of-pile sections. The loop is designed to utilize either pile radiation (reactor neutron and gamma energy), or the fission fragment energy of uranium containing alloy foils[25,26] which are especially fabricated to efficiently impart this energy into the radiation system.

A flowsheet of the chemonuclear loop is shown in Figure 2. Preliminary tests have been made of ozone yields from oxygen, using only pile neutron and gamma radiation.[27] In general, the results show that lower temperatures increase radiation yields and concentrations of ozone, as do higher pressures. It has also been found that the addition of nitrogen has a strong enhancing effect on the yield, depending on the system pressure and nitrogen concentration. Figure 3 shows a time history of a typical run in which an ozone concentration of 500 ppm was obtained despite the relatively low dose rate (2.4 megarads/hr) available from pile radiation. The integral G-value (radiation yield) for the 15.6% N_2 concentration was calculated to be in the order of 8 molecules/100 eV. Subsequent work has resulted in initial G-values as high as 12.

A summary of the radiation chemistry and chemonuclear loop results indicates the following:

1. G-value yields for ozone formation from oxygen can be obtained ranging from at least 10 to as high as 15.

2. There appears to be no effect of the type of radiation on the yield (no LET effect). Thus gamma radiation from sources such as Co^{60} and Cs^{137} or beta radiation from Sr^{90} and electron accelerators or fission fragments from direct fission of uranium should give similar yields of ozone.



FLOW SHEET

BROOKHAVEN CHEMONUCLEAR IN-PILE RESEARCH LOOP

FIGURE 2

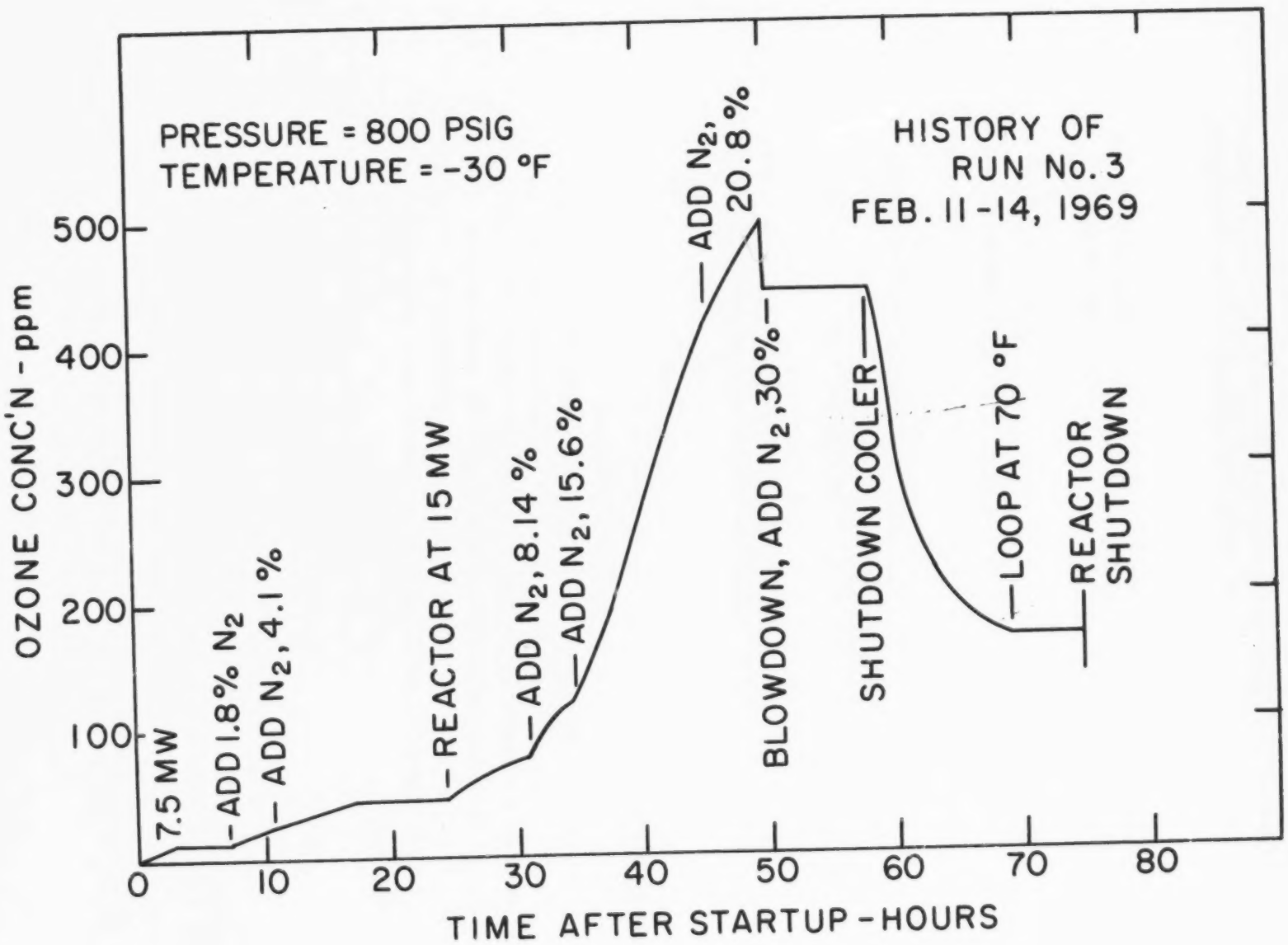

PRESSURE = 800 PSIG
TEMPERATURE = -30 °F
HISTORY OF
RUN No. 3
FEB. 11-14, 1969
OZONE CONC'N - ppm
TIME AFTER STARTUP - HOURS
0
10
20
30
40
50
60
70
80
100
200
300
400
500
7.5 MW
ADD 1.8% N2
ADD N2, 4.1 %
REACTOR AT 15 MW
ADD N2, 8.14 %
ADD N2, 15.6%
ADD N2, 20.8 %
BLOWDOWN, ADD N2, 30%
SHUTDOWN COOLER
LOOP AT 70 °F
REACTOR
SHUTDOWN

FIGURE 3

3. The steady state concentration of ozone is almost a direct function of the intensity. Concentrations as high as 0.5% have been obtained with fission fragment energy.

4. After conditioning the surface, ozone can be produced continuously in a steel processing system.

5. The yield and concentration of ozone tends to increase with pressure; tests up to 60 atm have been made.

6. The yield of ozone is favored by lower temperatures due to the thermal instability of ozone.[28] High yields have been obtained between -20 and 0°C.

7. Additions of nitrogen in the order of a few per cent by volume has a marked enhancing effect on the yield.

5.4 New Methods

In addition to isotopic and chemonuclear ozone development work, Brookhaven National Laboratory is also seeking to improve the electric discharge process. A promising method which combines both radiation and electric discharge is described in Appendix A. Lower energy requirements and higher yields are expected with this system.

5.5 PROCESS DESCRIPTIONS

5.5.1 Isotopic Process

Figure 4 is a flowsheet of an isotopic source ozone generator. Ozone generated as 1% by volume in an O_2-N_2 stream is sent to the Acid Mine Drainage (AMD) treatment plant for use in the ozone contactors, and the oxygen is recycled back to the ozone generator for re-use. The $30^{o}F$ temperature maintained by a refrigerated cooler results in higher ozone yields per unit of input energy.

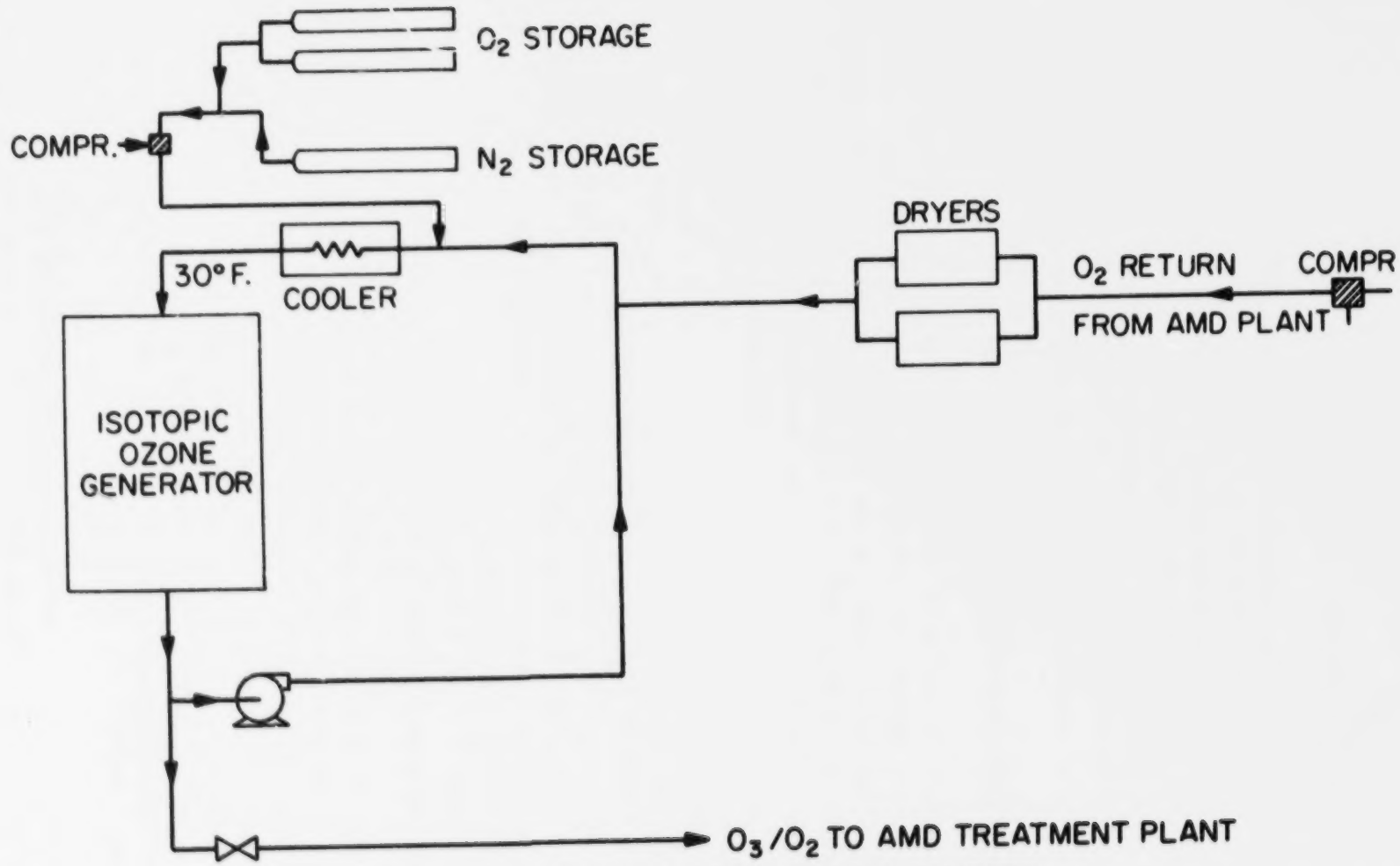
5.5.2 Electric Discharge Process

A similar flowsheet for the electric discharge ozonizer system is shown in Figure 5. Although an air separation plant is included, this would apply only to larger systems such as a 6×10^6 gal. per day AMD plant with high Fe^{++} contents, where ozone production in the order of 10 tons per day is required. Normally, oxygen gas from cylinders is employed, as in the isotopic source case. Ozone can also be produced by electric discharge through an air stream, thus eliminating oxygen recycle equipment. Since this requires higher energy input than with pure oxygen, the savings in recycling equipment may be offset by higher investment in ozonizers. The economics of both air and oxygen feed are discussed in a later section of the report.

5.5.3 Chemonuclear Process

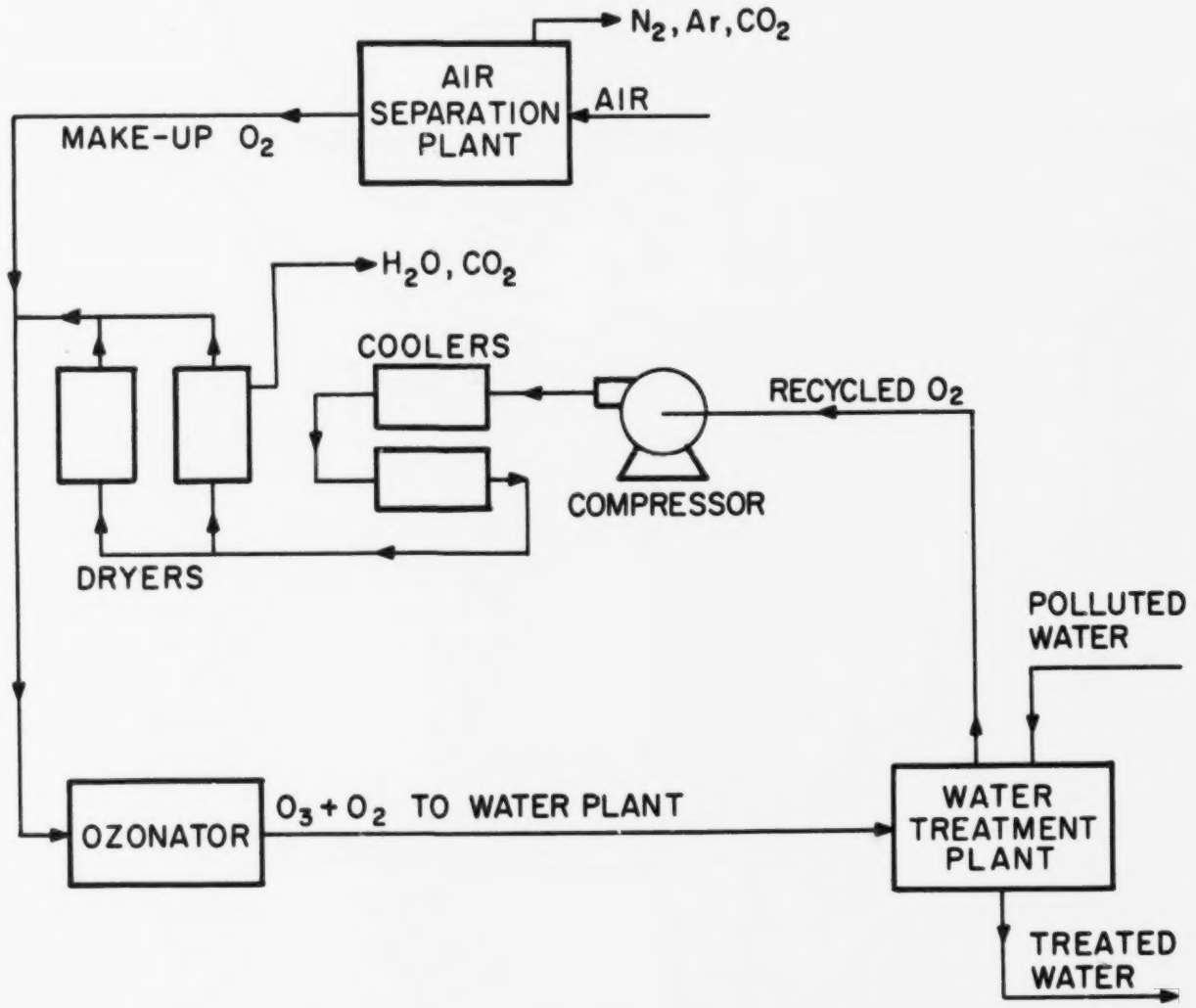
The third method of ozone production evaluated is the chemonuclear reactor, which employs the energy of nuclear fission to impart energy into reactant streams in the same manner as do gamma rays from isotopes. Since a nuclear reactor is employed as the energy source, the process is applicable to large-scale production. Thus, the method can be considered from a central production plant aspect only.

The chemonuclear method is illustrated in Figure 6. An oxygen-nitrogen stream from an air-separation plant is passed through a critical array of specially designed fuel elements.[25] The fuel consists of uranium-aluminum alloy assemblies coated on an aluminum plate substrate.



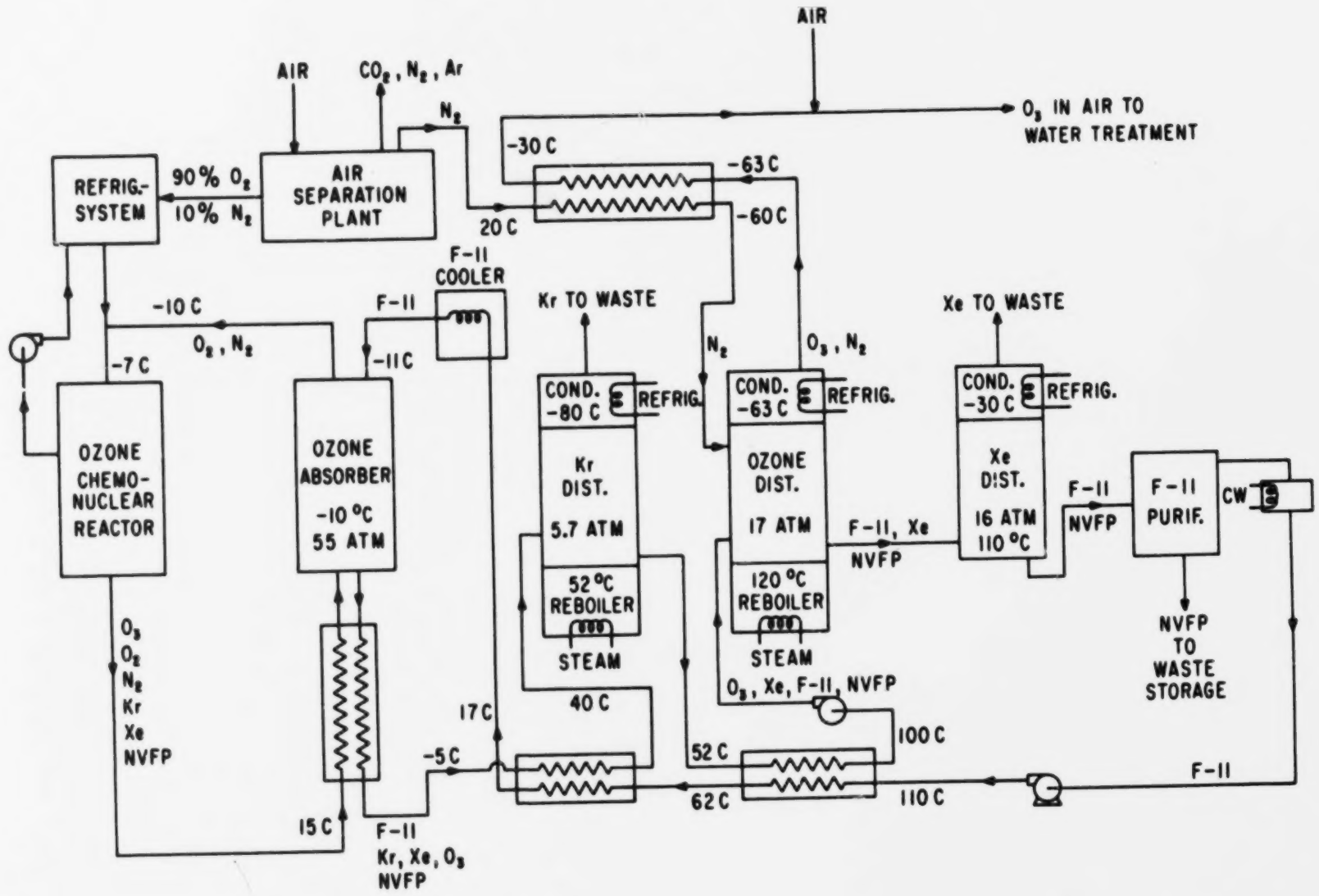
OZONE GENERATION USING ISOTOPIC SOURCES

FIGURE 4



ELECTRICAL DISCHARGE OZONE PROCESS
FOR WATER TREATMENT

FIGURE 5



CHEMONUCLEAR OZONE GENERATION AND PURIFICATION FOR WATER TREATMENT

FIGURE 6

The alloy coating is only 0.25 mil thick, and would release at least 20% of the fission fragment energy into the reactant gas, which is maintained at a 30°F average temperature.

A major potential problem in the process is the removal of fission products from the ozone-containing gas stream, particularly the volatile noble gases krypton and xenon. The non-volatile solid fission products are physically removed by deposition on surfaces and by filtration. The volatile gases may be removed by a Freon absorption-stripping system,[29] as shown in Figure 6. This is a multi-column separation scheme which depends upon the solubility of krypton and xenon in Freon at low temperatures, which are fairly high. This type of system has been shown to be feasible for nuclear fuel reprocessing plants.[29,30]

BLANK PAGE

6. ECONOMIC ANALYSIS

6.1 ON-SITE PLANTS

6.1.1 Isotopic Process

Because of its limited capacity the Isotopic Process lends itself mainly for applications to on-site treatment plants.

The isotopes chosen for evaluation were ^{60}Co and ^{137}Cs. ^{60}Co is presently used widely in radiation processing. ^{137}Cs is under development as a radiation source, and could become available at low cost since it is a by-product of the nuclear power industry. For this study, the source types produced at BNL, described in Table 5, were used as reference sources. The generator concept is that of a vessel, as shown in the sketch in Figure 8, with the sources arrayed in a circular pattern inside the vessel. The optimum arrangement to provide minimum energy loss, both to the vessel walls and to other sources, is that the source array have a diameter one-third that of the vessel. The amount of energy deposited in the reactant stream flowing through the vessel is a function of the pressure, since higher pressures result in a denser medium which captures more energy, thus is more efficient from an energy standpoint. This is counterbalanced by the greater cost of high-pressure vessels, compression equipment, and power requirements. The analysis is then one of optimization. Figure 7 shows the energy deposition from ^{60}Co and ^{137}Cs at various pressures through different thicknesses of oxygen layers, and is a guide for selecting pressure vessel diameter.

Isotope requirements can be calculated from the equations:

$$C = \frac{6850T}{GEM} \text{ for } ^{60}Co$$

$$C = \frac{26{,}000T}{GEM} \text{ for } ^{137}Cs$$

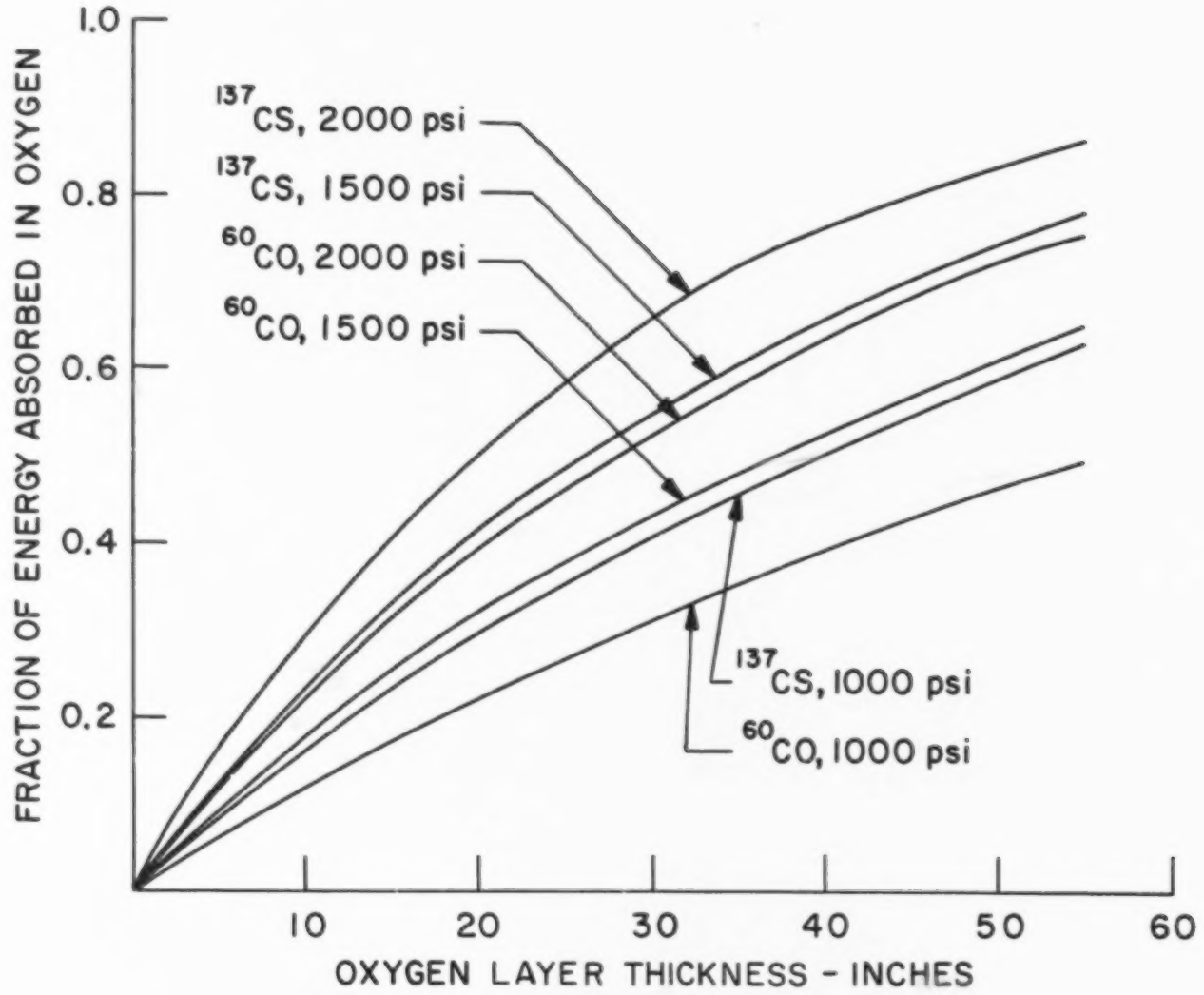
PRECEDING PAGE BLANK

TABLE 5

CHARACTERISTICS OF BNL GAMMA SOURCES

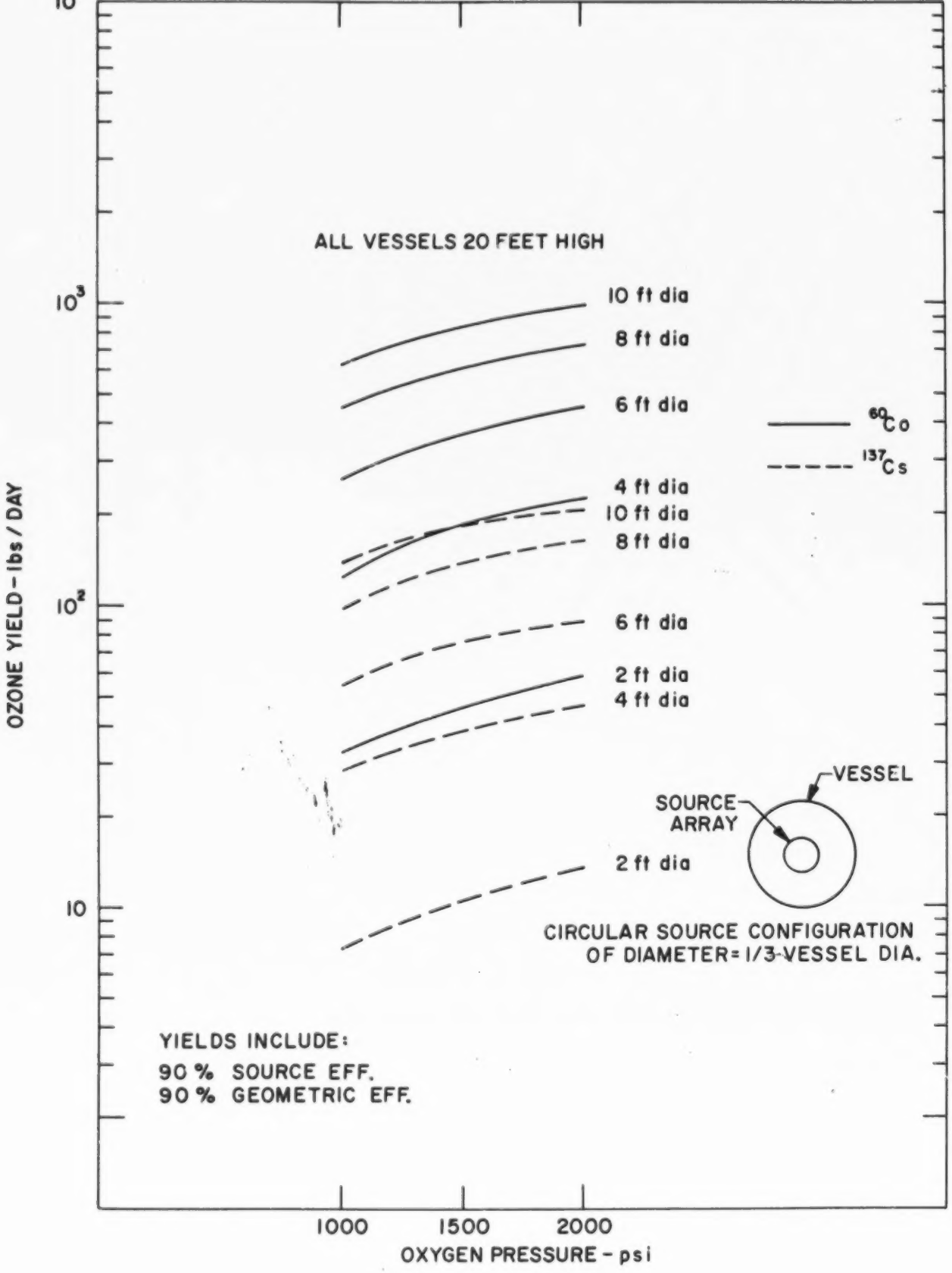
	^{60}Co	^{137}Cs
Power, Curies	5,000	4,000
Size, in.	13-1/16 x 0.70 x 1/8	13¼ x 1-1/8 x 3/8
Half-life, yrs.	5.3	30
Gamma Energy, MeV	2.5	0.66
Cross-Section, cm^2/g	0.055	0.078
Heat Generation, w/KCi	14.8	5.0

PRECEDING PAGE BLANK



GAMMA-RAY ENERGY ABSORPTION IN O_2 VS
PATH LENGTH AT HIGH PRESSURE

FIGURE 7



OZONE YIELD vs OXYGEN
PRESS. FOR VESSELS OF VARYING DIAMETERS.

FIGURE 8

C = Amount of isotope required, megacuries

T = Ozone production quantity, tons/day

G = G value for energy absorbtion, molecules/100 eV

E = Energy deposition efficiency in gas, a fraction

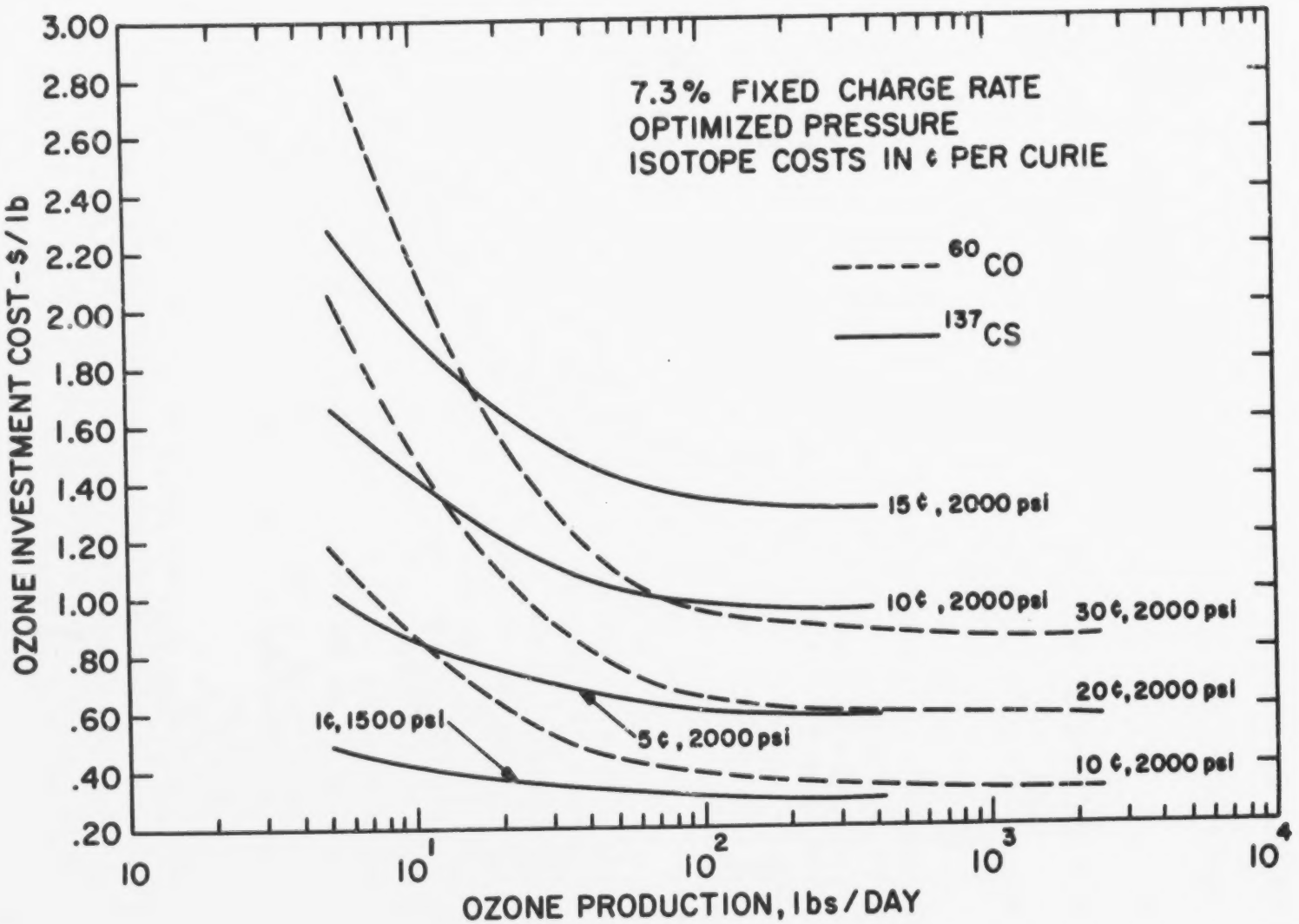
M = Molecular weight of product (O_3 = 48)

The capacity of ozone obtainable for different vessel diameters and pressures is shown in Figure 8. Costs of pressure vessels, compressors and isotopes were estimated for the various sizes and pressures, and it was found that for the cases where large ozone quantities are required, 10 ft dia. vessels are optimum, and multiple vessels were generally required to meed the demands of most cases. In addition to the above-mentioned costs, costs of shielding for radiation protection, installation, and isotope investment and replacement were factored in. For ^{60}Co, costs of 10, 20, and 30¢ per Ci were chosen. Present day costs are about 30¢ per Ci for large quantities, and it was assumed that as usage increased, cost would decrease. ^{137}Cs was assumed to cost 1, 5, 10 and 15¢ per Ci. These low costs may not be unreasonable, since ^{137}Cs may become readily available in the near term from nuclear power fuel reprocessing plants at low cost due to the problem of long-term disposal of the isotopes from spent fuel elements. It is conceivable that ^{137}Cs may be obtained by mere payment of the shipping costs.

Figure 9 shows the depreciation of the investment costs (at 7.3% depreciation rate) expressed in dollars/lb. ozone for the isotopes, Figures 10 and 11 show the production costs of ozone by this method, and Figure 12 expresses the lowest ozone production costs from isotopes in dollars per 1000 gal. This production cost includes depreciation, operating costs, and oxygen cost. Note that this is the cost of ozone production only, and does not include the AMD treatment plant.

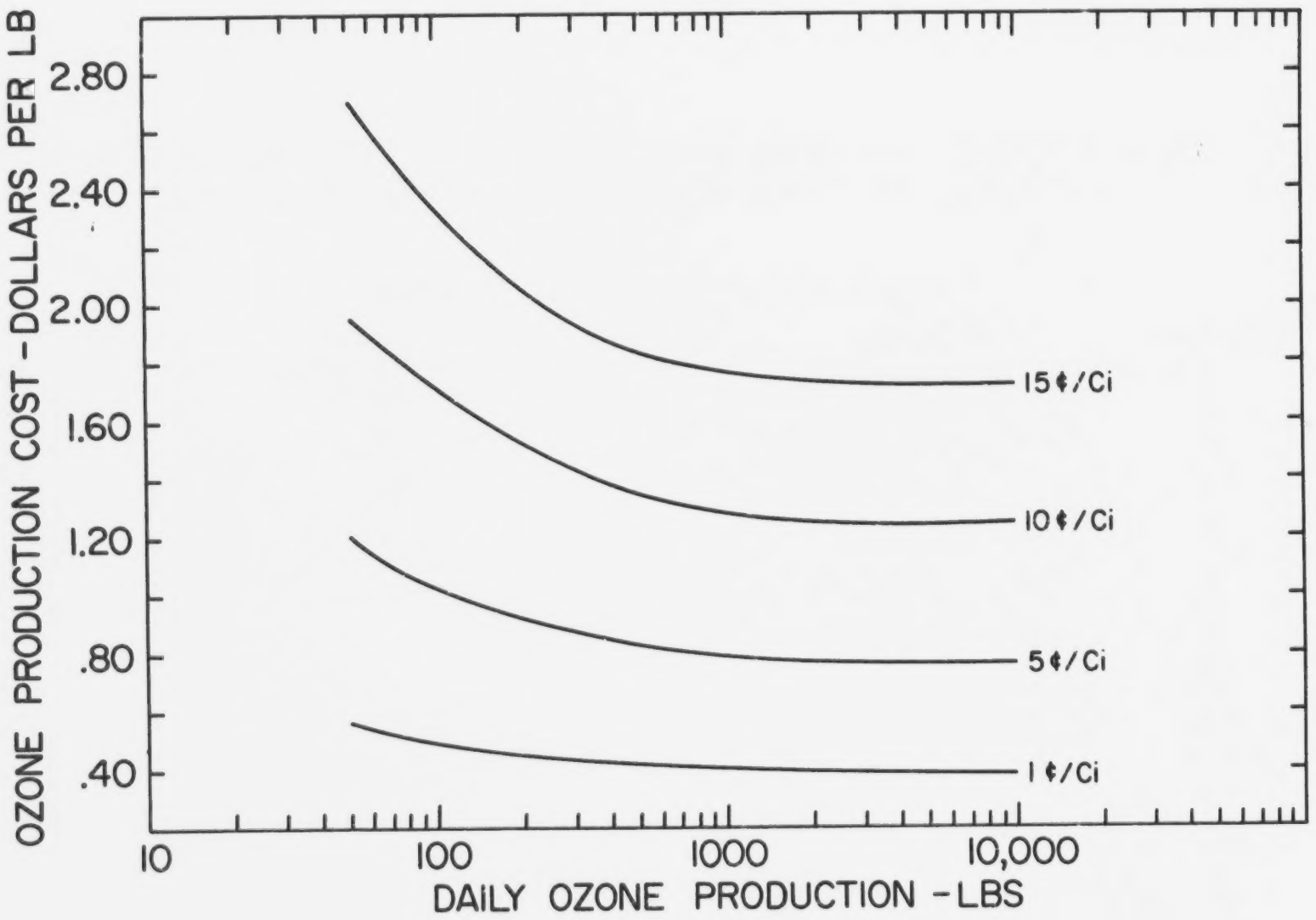
The ozone cost for water treatment is obtained from the equation:

$$T = \frac{LP}{W}$$



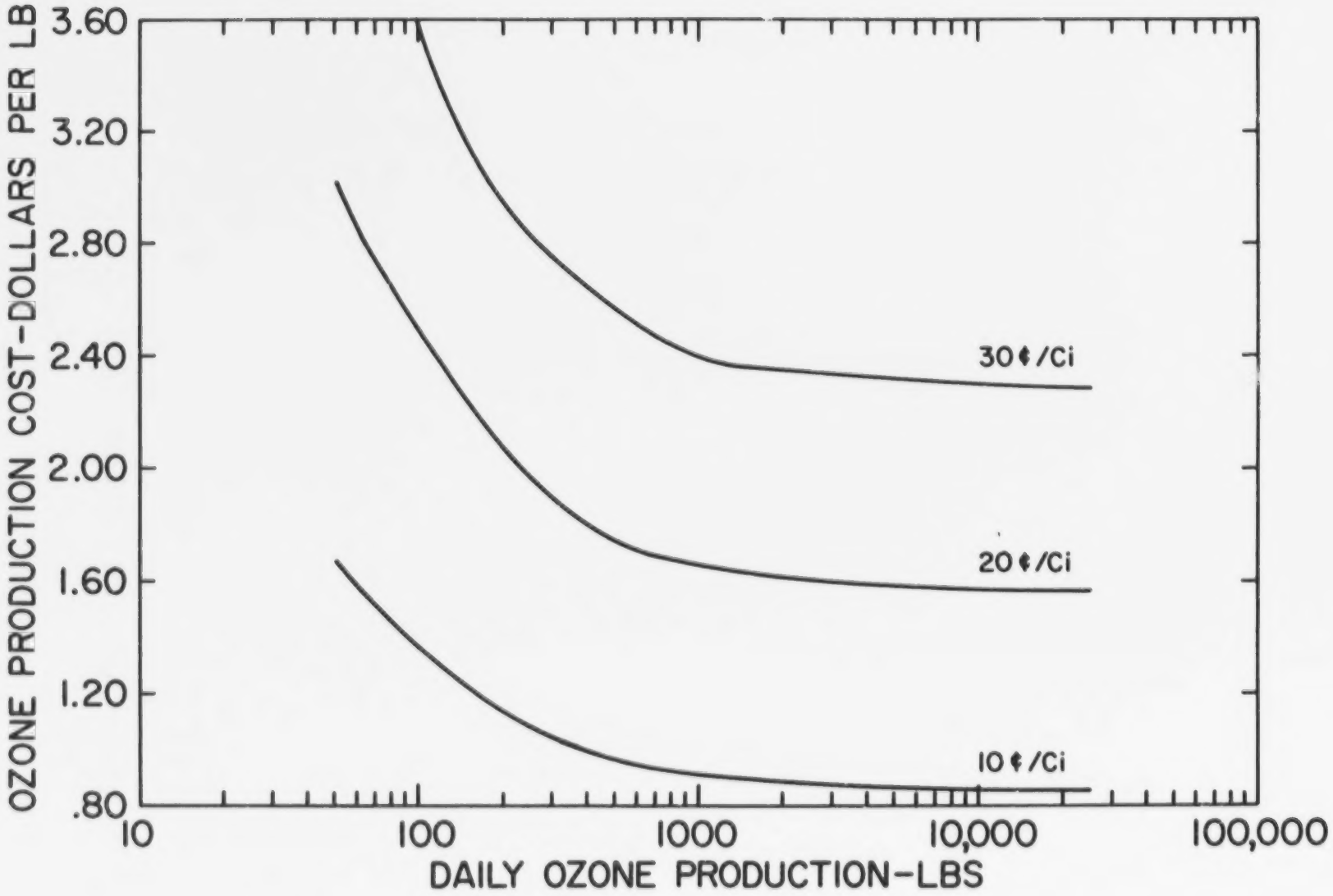
INVESTMENT COSTS FOR OZONE
USING ISOTOPIC RADIATION

FIGURE 9



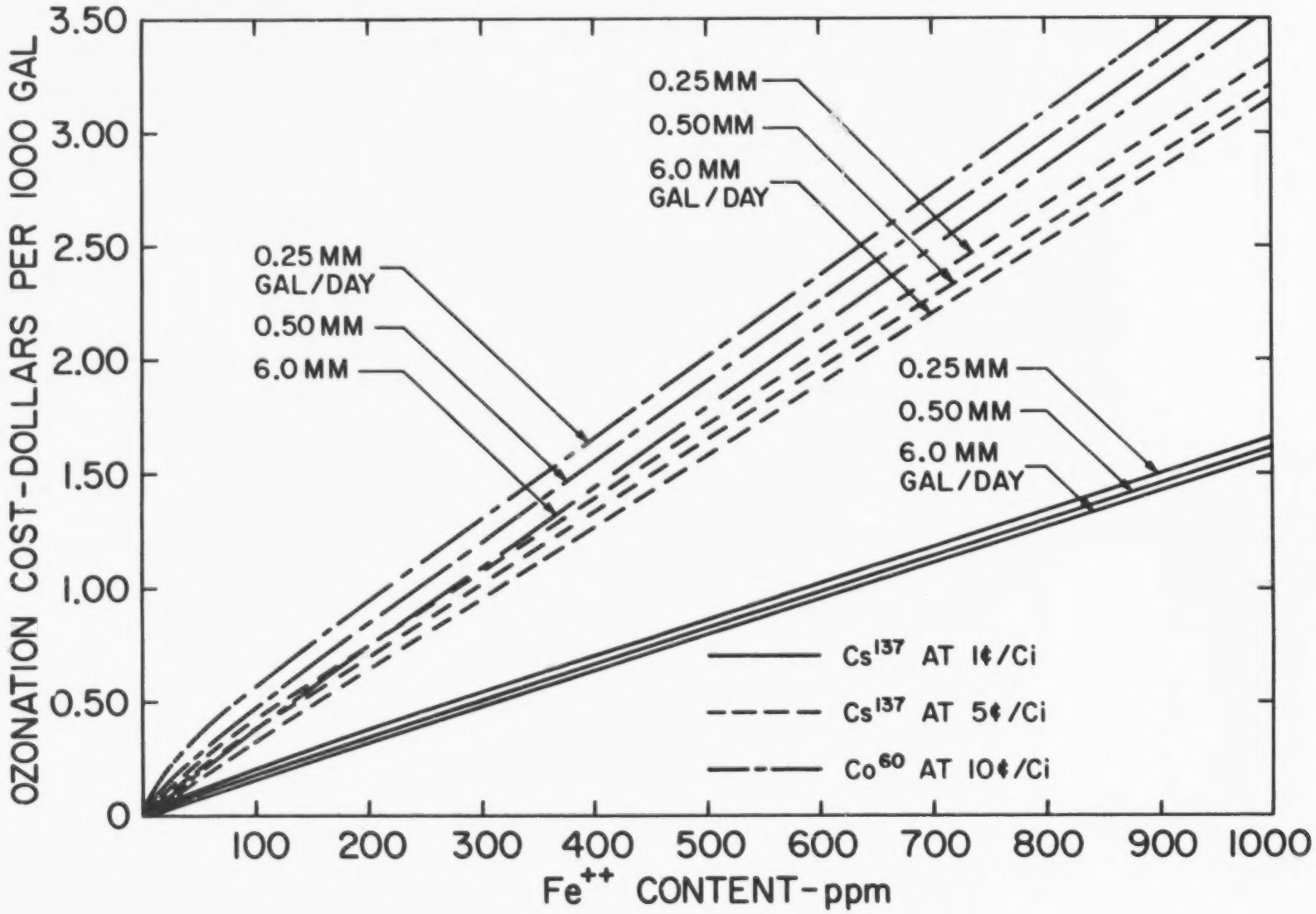
CESIUM-137 OZONE GENERATOR, 1500-2000 psi PRESSURE
PRODUCTION COST vs CAPACITY FOR VARYING SOURCE COSTS

FIGURE 10



COBALT-60 OZONE GENERATOR, 2000 psi PRESSURE
PRODUCTION COST vs CAPACITY FOR VARYING SOURCE COSTS

FIGURE 11



ISOTOPIC SOURCE OZONIZERS, COST OF AMD OZONATION AT VARYING DAILY STREAM FLOWS AND Fe^{++} CONTENTS-OXYGEN FEED AND RECYCLE

FIGURE 1 2

where:

T = ozone cost, ¢/1000 gal.

P = ozone cost, ¢/lb.

L = ozone required, lbs/day

W = AMD flow, thousand of gal./day

All production costs in this study were based on an annual fixed charge rate of 7.3%, which is commonly used by utility-type industries.

It is readily apparent that this method is a relatively high cost system; despite the high efficiency, the large investment necessary (mainly in isotopic sources) and the high replacement cost for isotopic decay offers little inducement for development of this method for large-scale use in this particular application, except possibly for very low Fe^{+2} AMD streams. For example, the investment cost for ozone production for a 250,000 gpd AMD plant at a Fe^{+2} concentration of 300 ppm is $664,000 using ^{60}Co at 10¢ per Ci, or $479,000 using ^{137}Cs at 1¢ per Ci. Later in this report, it will be seen that the came capacity can be handled by electric discharge units for an investment cost of $60,000.

The isotopic process may become interesting for treatment of acid mine drainage for Fe^{+2} contents below 50 ppm. The only advantage of an isotope source is that no primary power supply is required. ^{137}Cs isotope has a half life of 30 years, and thus plant life is long. However, auxiliary power from pumps and compressors would be required.

6.1.2 Electric Discharge Process

For on-site AMD treatment plants, with ozone produced at the site, the electric discharge method is a feasible process. The largest usage at one site considered in this study requires 12.5 tons per day ozone to treat 6 million gal. AMD containing 1000 ppm Fe^{++}, and the smallest, for treatment of 250,000 gal. per day with a Fe^{++} content of 50 ppm, requires only 52 lb per day ozone. Both once-through air feed and recycled oxygen feed were considered in the evaluation. Investment and production costs for both methods are listed in Table 6 through 9, and the data is plotted in Figures 13, 14 and 15 in terms of ozone cost per lb and per 1000 gal. AMD. Note once again that these are only the costs of ozone production, and do not include the AMD treatment plant itself. These are evaluated later in the report. Costs of ozonizers and auxiliary equipment were obtained from a commercial ozone equipment manufacturer.(32) Cost of purchased oxygen was obtained from Linde Co.(33) Purchased oxygen was assumed in all oxygen cases except the 25,000 lb per day ozone plant, where the cost is based on an on-site oxygen plant, since the saving to be gained is very significant. The cost of purchased oxygen is given in Table 10. The oxygen plant results in a saving of about 1¢ per lb ozone, which reduces annual operating costs by $75,000.

Once-through air feed ozonizers are more economical at capacities up to about 200 lb per day. This occurs because the higher investment cost for ozonizers is overridden by the high purchase cost of oxygen at low capacities. Above 200 lb per day ozone requirement, the recycled oxygen system is the choice.

TABLE 6

OZONE INVESTMENT COSTS

ON-SITE GENERATION, ONCE-THROUGH AIR FEED

Cost in Thousands of Dollars

Lb/Day Ozone	50		1000		7500		25,000	
Energy Req't. KW-Hr/lb.	7.25	9.75	7.25	9.75	7.25	9.75	7.25	9.75
Ozonizers	7.5	7.5	118	140	620	780	1,720	2,240
Auxiliaries	3.9	5.2	48	65	159	214	410	550
Construction	3.5	4.7	44	59	135	180	400	530
Total Investment	14.9	17.4	210	264	914	1,174	2,530	3,320

TABLE 7

OZONE PRODUCTION COSTS

ON-SITE GENERATION, ONCE-THROUGH AIR FEED

Costs in ¢/lb

Lb/Day Ozone	50		1,000		7,500		25,000	
Energy Req't, Kw-Hr/lb.	7.25	9.75	7.25	9.75	7.25	9.75	7.25	9.75
Depreciation	7.27	8.50	5.12	6.44	2.97	3.82	2.47	3.24
Labor	1.80	1.80	1.80	1.80	1.80	1.80	1.80	1.80
Maintenance	1.80	1.80	1.80	1.80	1.80	1.80	1.80	1.80
Power*	6.20	8.20	6.20	8.20	6.20	8.20	6.20	8.20
Total	17.07	20.30	14.92	18.24	12.77	15.62	12.27	15.04

*Includes additional 0.5 KW-Hr/lb for auxiliaries.

TABLE 8

OZONE INVESTMENT COSTS

ON-SITE GENERATION, RECYCLED OXYGEN FEED

Cost in Thousands of Dollars

Lb/Day Ozone	50		1000		7500		25,000	
Energy Req't, KW-Hr/lb.	3.75	5.00	3.75	5.00	3.75	5.00	3.75	5.00
Ozonizers	3.75	5.00	65.0	86.5	353	470	950	1265
Auxiliaries	4.00	5.35	50.0	66.5	165	220	425	565
Construction	2.00	2.67	25.0	33.3	90	120	225	300
Total	9.75	13.02	140.0	186.3	608	810	1600	2130
Oxygen Plant	--	--	--	--	--	--	350	350
Total with Oxygen Plant	--	--	--	--	--	--	1950	2480

TABLE 9

OZONE PRODUCTION COSTS

ON-SITE GENERATION, RECYCLED OXYGEN FEED

Cost in ¢/lb

Lb/Day Ozone	50		1000		7500		25,000	
Energy Req't, KW-Hr/lb.	3.75	5.00	3.75	5.00	3.75	5.00	3.75	5.00
Depreciation	4.75	6.36	3.42	4.55	1.98	2.64	1.56	2.08
Labor	1.20	1.20	1.20	1.20	1.20	1.20	1.20	1.20
Maintenance	1.20	1.20	1.20	1.20	1.20	1.20	1.20	1.20
Oxygen	12.60	12.60	4.00	4.00	2.00	2.00	0.60	0.60
Power*	3.83	4.82	3.83	4.82	3.83	4.82	4.00	5.00
	23.58	26.18	13.65	15.77	10.21	11.86	8.56	10.08

*Includes additional 1.04 KW-Hr/lb for auxiliaries, and 1.25 KW-Hr/lb for 25,000 Lb/Day plant case where oxygen plant is used.

TABLE 10

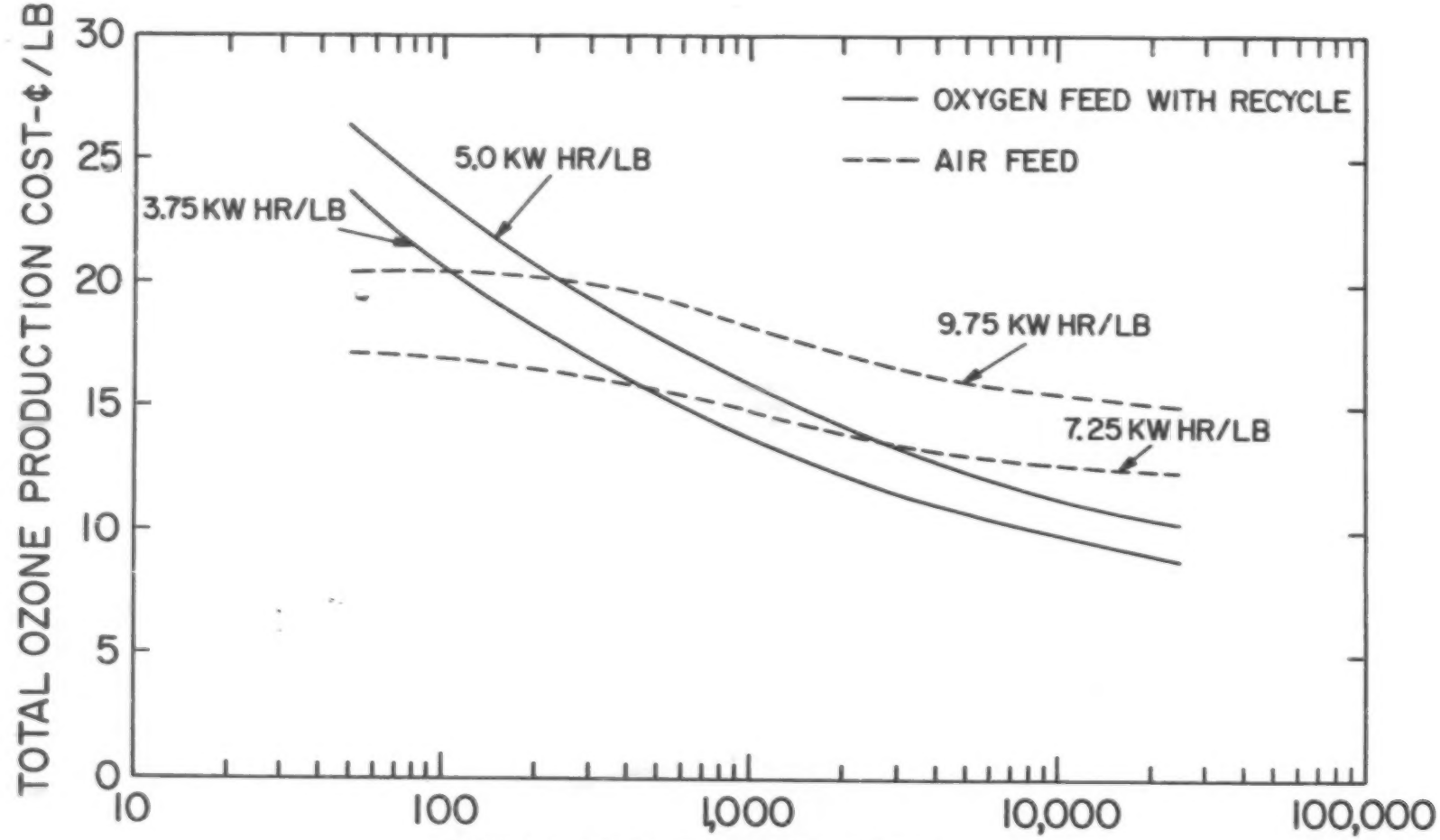
COST OF PURCHASED OXYGEN GAS*

Monthly Usage

1st 20,000 ft^{3}**	$1.05/100 ft^{3}**
Next 60,000	.50 "
Next 120,000	.33 "
Next 800,000	.17 "
Over 1,000,000	.13 "

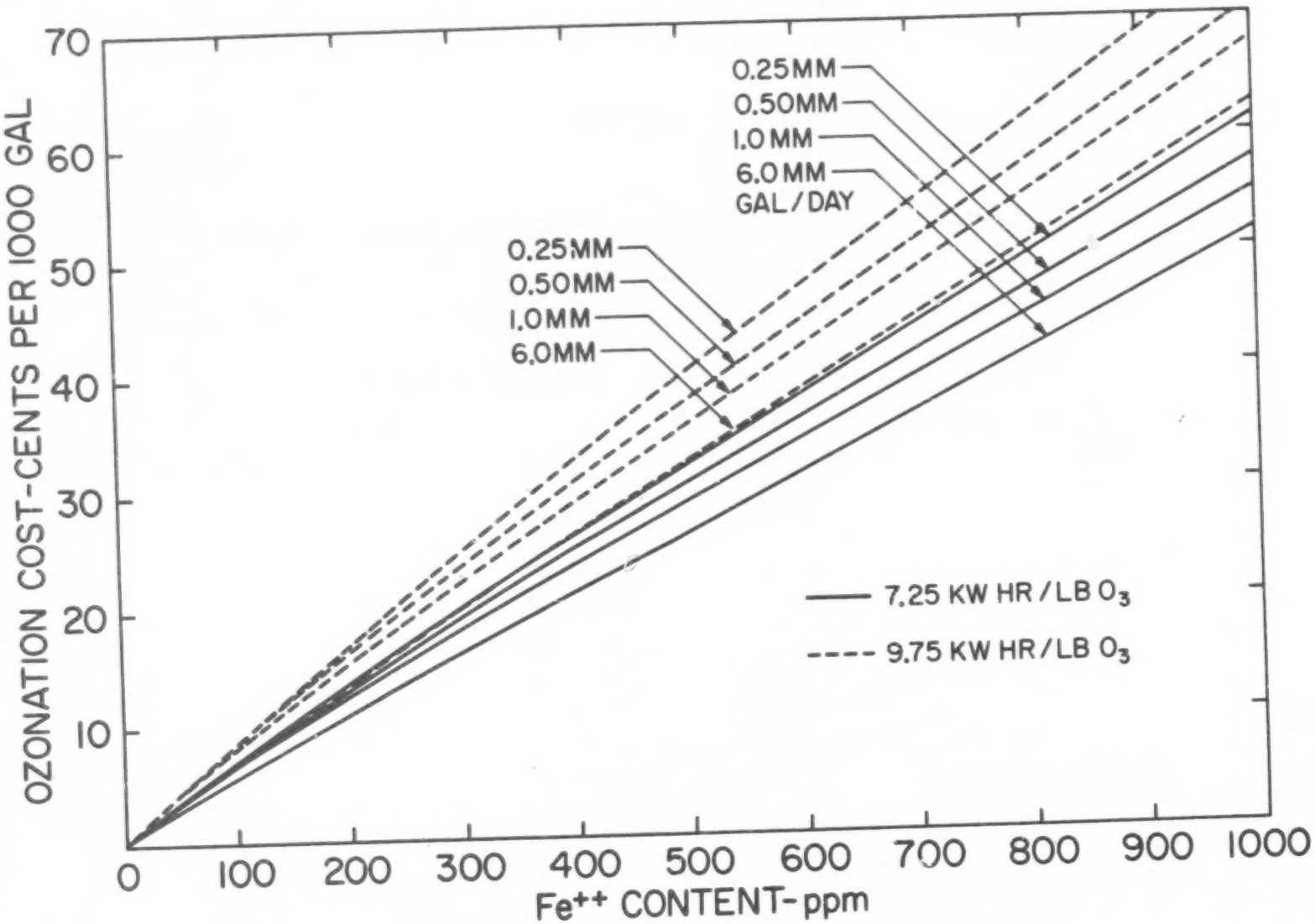
*From Linde Co., Div. Union Carbide Corp.

**Ft^{3} expressed at 70^{o}F, 1 ATM.



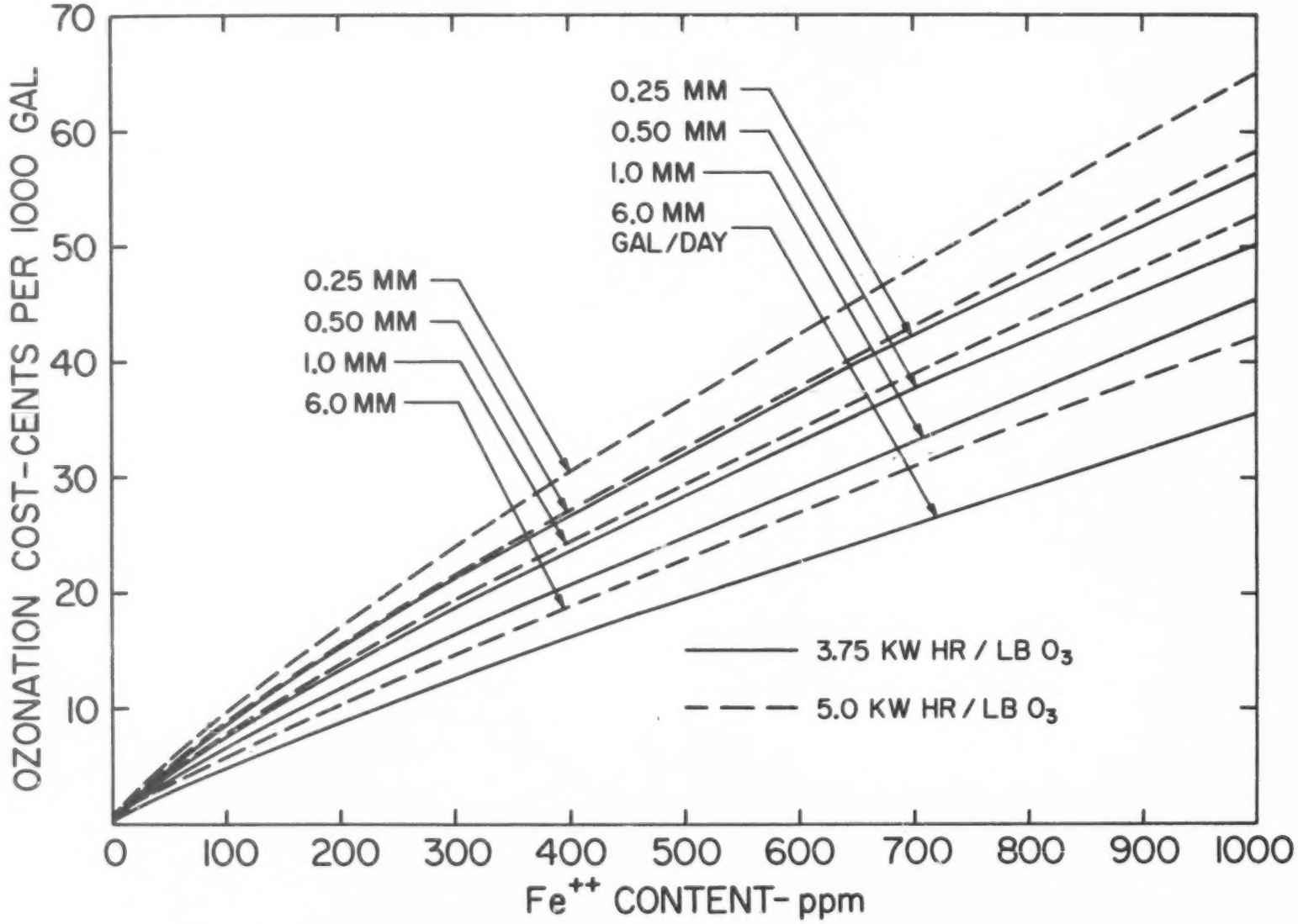
ELECTRIC-DISCHARGE OZONIZERS, PRODUCTION COST vs CAPACITY AT VARIOUS POWER CONSUMPTIONS, AND FOR OXYGEN AND AIR FEEDS

FIGURE 13



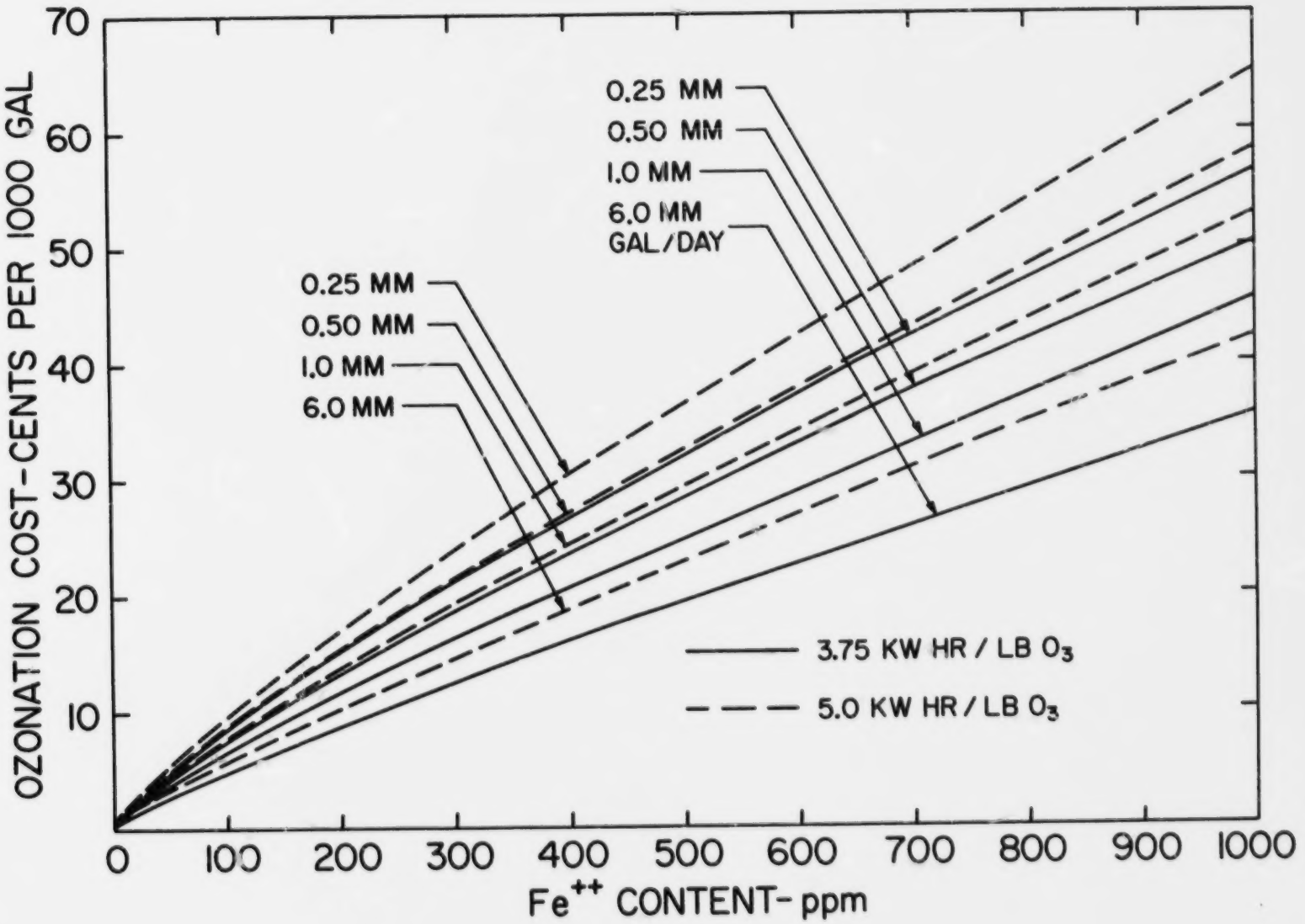
ELECTRIC DISCHARGE OZONIZERS, COST OF AMD OZONATION AT VARYING DAILY STREAM FLOWS AND Fe^{++} CONTENTS - ONCE THROUGH AIR FEED

FIGURE 14



ELECTRIC DISCHARGE OZONIZERS, COST OF AMD OZONATION AT VARYING DAILY STREAM FLOWS AND Fe^{++} CONTENTS - OXYGEN FEED AND RECYCLE

FIGURE 15



ELECTRIC DISCHARGE OZONIZERS, COST OF AMD OZONATION AT VARYING DAILY STREAM FLOWS AND Fe^{++} CONTENTS - OXYGEN FEED AND RECYCLE

FIGURE 15

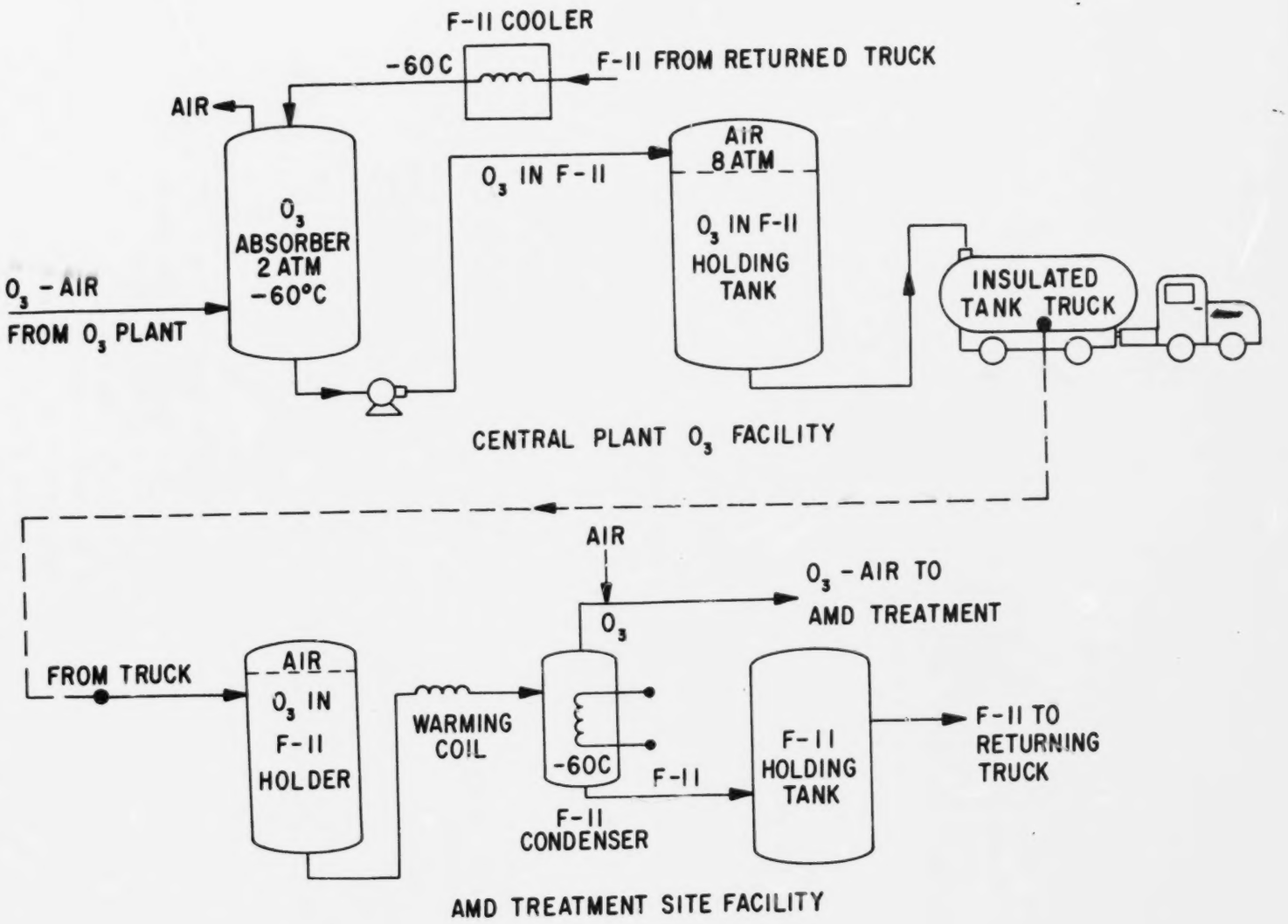
6.2 CENTRAL OZONE PRODUCTION PLANTS

6.2.1 Ozone Shipping and Storage

Economies can be achieved for most chemicals by large-scale central facilities, and ozone is no exception. However, the problem of storage and shipment to usage points has generally discouraged efforts to generate ozone except at the point of use. In the last few years, some producers of industrial gases have started to ship ozone, dissolved in Freon solvents, on a small scale. When ozone is dissolved in Freon at moderately low temperatures, the storage life and stability of the compound are greatly enhanced. By this method, ozone can be shipped in interstate commerce. Enlarging upon existing technology, a method for large-scale ozone shipment was devised, as shown in Figure 16. The ozone-air mixture from the central ozone plant is stripped of air in a Freon-11 absorber at -60°C. The ozone, now dissolved in Freon-11, is kept in a holding tank for distribution in insulated tank trucks, similar to those used for distribution of liquified natural gas and nitrogen. The truck delivers the ozone to the AMD site, where the ozone-Freon mixture is transferred to an insulated storage tank. As the ozone is required for AMD treatment, it is withdrawn through a warming coil, in which ozone and some Freon is flashed. In a partial condenser, the flashed Freon is recondensed, and the ozone gas is mixed with air and passes to the AMD contactors. Condensed F-11 is returned to the central ozone plant in the now empty tank truck.

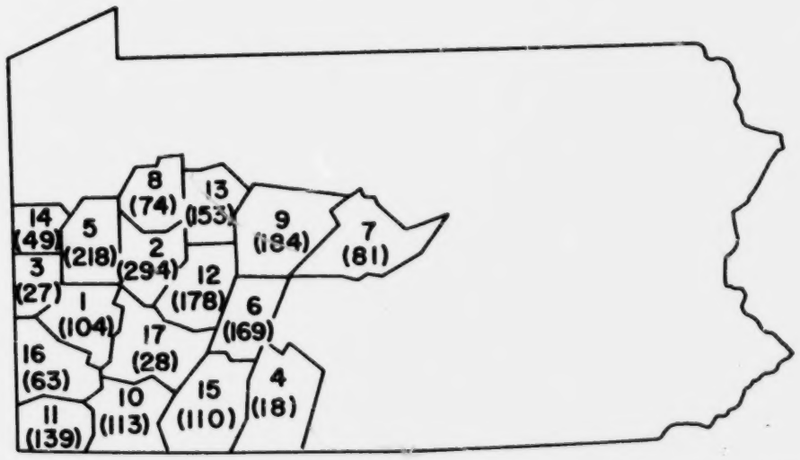
Figure 17 illustrates how ideally the central plant distribution system fits the Pennsylvania AMD situation. The map shows where the coal-mine drainage counties are located, and also shows the number of draining mines[34] in each county. The geography is such that the shipping distance ranges from a radius of 60-75 miles maximum from a central plant located in Indiana County. This would also offer the possibility of obtaining mine-mouth power from the Keystone generating station. In this case, favorable off-peak power rates for the continuously operating ozone plant might be obtained.

PRECEDING PAGE BLANK



OZONE STORAGE AND DISTRIBUTION SYSTEM

FIGURE 16



NUMBER IN PARENTHESIS IS NO. OF DRAINING MINES
(DATA FROM PENNA. DEP'T OF HEALTH)

COUNTY KEY

1. ALLEGHENY
2. ARMSTRONG
3. BEAVER
4. BEDFORD
5. BUTLER
6. CAMBRIA
7. CENTRE
8. CLARION
9. CLEARFIELD
10. FAYETTE
11. GREENE
12. INDIANA
13. JEFFERSON
14. LAWRENCE
15. SOMERSET
16. WASHINGTON
17. WESTMORELAND

DISTRIBUTION OF DRAINING COAL MINES IN PENNSYLVANIA COUNTIES

FIGURE 17

Data from the Pennsylvania Department of Health[34] show 2,158 known draining coal mines in the state. Their total flow is 486 x 10^6 gallons per day, or an average flow of approximately 250,000 gal. per day. Their average Fe^{++} content is about 200 ppm. To treat the total quantity requires an ozone plant with approximately 200 tons per day capacity.

6.2.2 Chemonuclear Process and Comparison with Electric Discharge Process

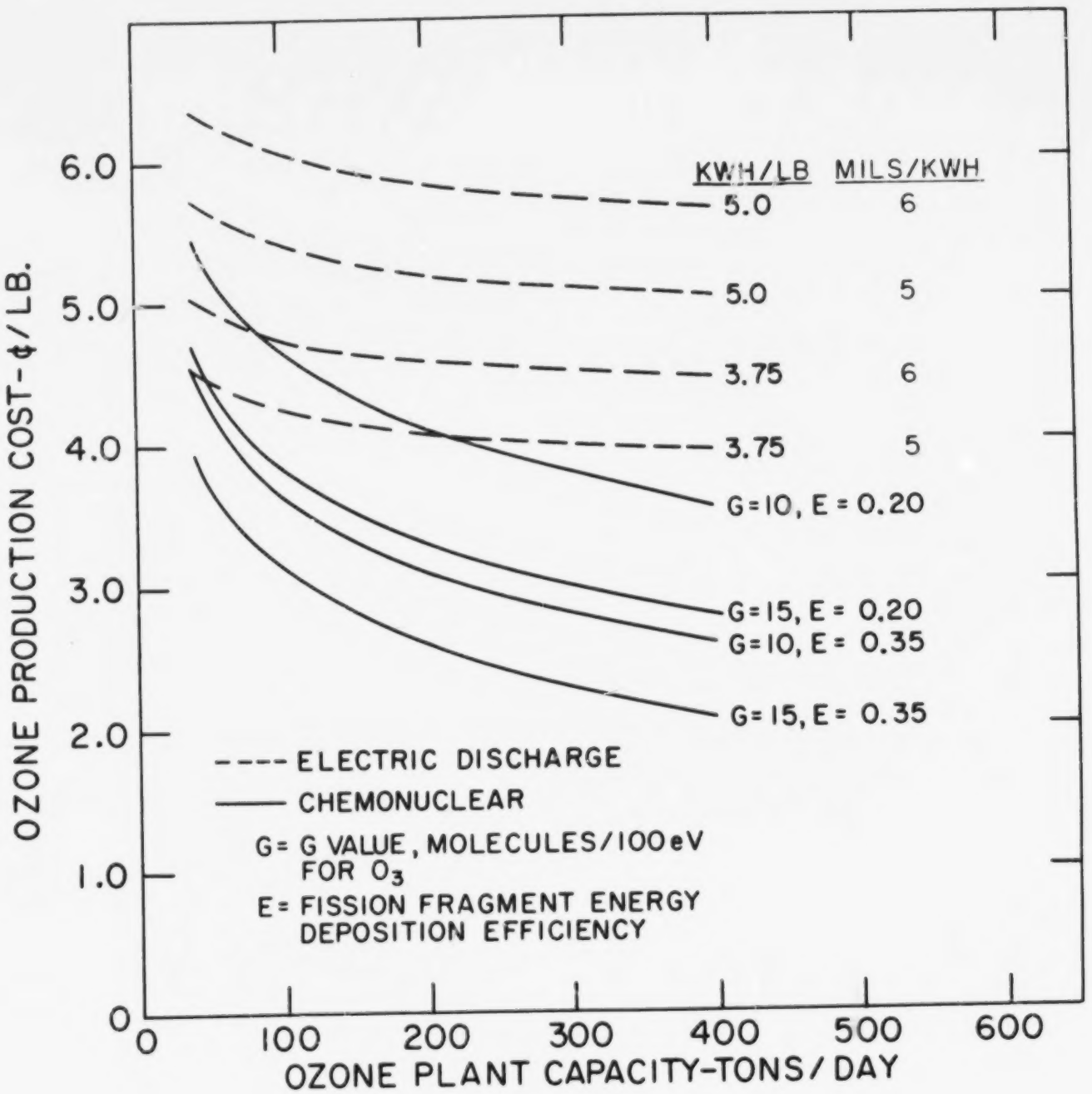
Cost estimates were made of central ozone generating plants ranging from 40 to 400 tons per day. Electric discharge and chemonuclear methods were compared, and the ozone costs are shown in Figure 18. In terms of ozone cost for water treatment, the results are shown in Figure 19 at various plant capacities. Two power costs are shown for the electric discharge case; because of the large power requirement, this variable strongly affects electric discharge economics. Figure 19 also assumes a 5.0 kw-hr/lb. power consumption. For the chemonuclear cases, Figure 19 shows the least efficient (i.e., most conservative) combinations of G-value and energy deposition efficiency. Investment and operating costs for these cases are itemized in Table 1 through 14 and energy requirements in Tables 15 through 18.

The definite advantage of chemonuclear over electric discharge is readily apparent from Figure 19. For example, taking the 200 ton/day ozone case, which would serve all of Pennsylvania's AMD treatment requirements (486 x 10^6 gal/day), and the average Fe^{+2} content of 200 ppm, the most conservative electric discharge ozone cost (6 mil power) is 5¢/lb ozone. For the same case, the most conservative chemonuclear cost (G=10,E=20) is 3¢/lb, thus resulting in a 40% saving in ozone production cost.

The basis for the estimates are as follows:

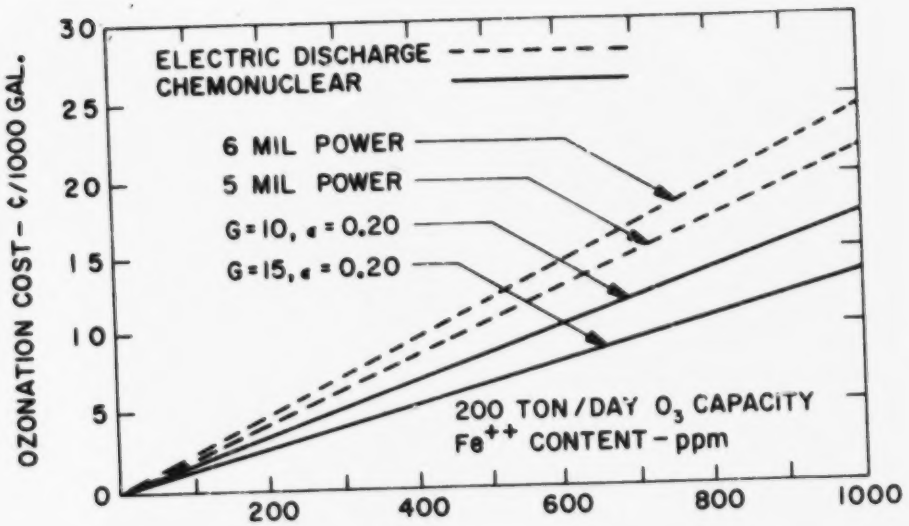
Chemonuclear Case - Fission Fragment Reactor

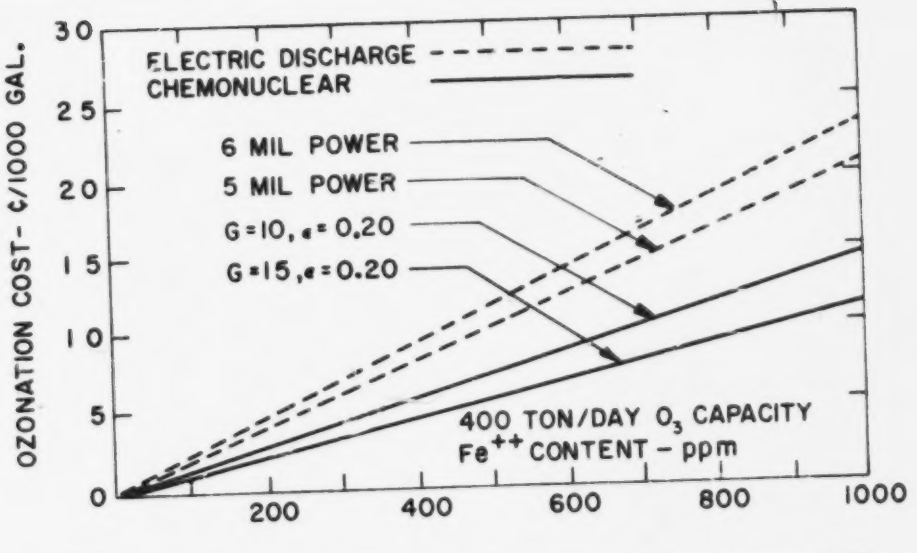
1. 20% of the reactor heat is removed by recycle gas refrigeration, and the remainder by cooling water.

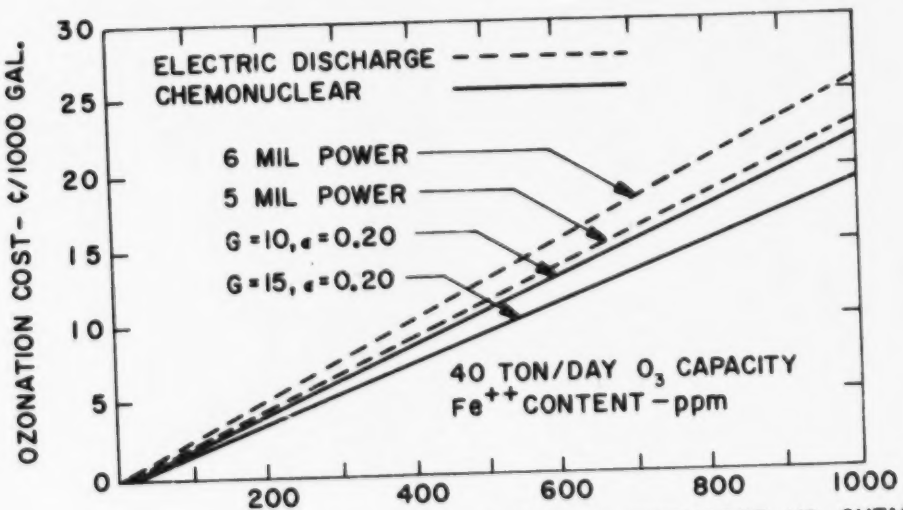


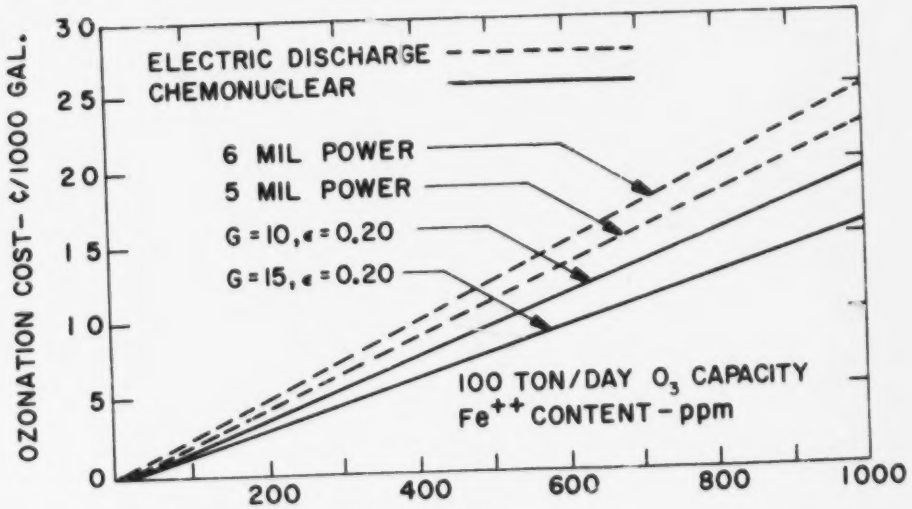
PRODUCTION COST OF OZONE,
CONVENTIONAL vs CHEMONUCLEAR PROCESSES

FIGURE 18









ELECTRIC DISCHARGE VS. CHEMONUCLEAR AMD TREATMENT COSTS USING OZONE FROM LARGE CENTRAL PLANTS (OZONE PRODUCTION COST ONLY)

FIGURE 19

TABLE 11

CHEMONUCLEAR OZONE

TOTAL PRODUCTION COST - ¢/LB O_3

T - Capacity Ton O_3/Day	40		40	
G - Values, Molecules/100 eV	10		15	
E - Energy Deposition Efficiency	0.20	0.35	0.20	0.35
P - Power Level of Reactor, MW(t)	42.5	24.2	28.3	16.1
Depreciation @ 7.3%	2.36	2.33	2.33	2.28
Nuclear Fuel Cycle	1.30	0.80	0.90	0.50
Labor	0.50	0.50	0.50	0.50
Maintenance	0.16	0.16	0.16	0.16
Power	1.14	0.72	0.81	0.53
Total - ¢/lb. O_3	5.46	4.51	4.70	3.97

T - Capacity, Tons/Day	100		100	
G - Values, Molecules/100 eV	10		15	
E - Energy Deposition Efficiency	0.20	0.35	0.30	0.35
P - Reactor Power, MW(t)	106	60.5	71.0	40.0
Depreciation @ 7.3%	1.84	1.76	1.77	1.73
Nuclear Fuel	1.30	0.80	0.90	0.50
Labor	0.25	0.25	0.25	0.25
Maintenance	0.12	0.12	0.12	0.12
Power	1.14	0.72	0.81	0.53
Total, ¢/lb. O_3	4.65	3.65	3.85	3.13

T - Capacity Ton O_3/Day	200		200	
G - Values, Molecules/100 eV	10		15	
E - Energy Deposition Efficiency	0.20	0.35	0.20	0.35
P - Power Level of Reactor, MW(t)	212	121	142	80
Depreciation @ 7.3%	1.42	1.35	1.36	1.32
Nuclear Fuel	1.30	0.80	0.90	0.50
Labor	0.16	0.16	0.16	0.16
Maintenance	0.10	0.10	0.10	0.10
Power	1.14	0.72	0.81	0.53
Total - ¢/lb. O_3	4.12	3.13	3.33	2.61

T - Capacity, Tons/Day	400		400	
G - Values, Molecules/100 eV	10		15	
E - Energy Deposition Efficiency	0.20	0.35	0.20	0.35
P - Reactor Power, MW(t)	424	242	284	160
Depreciation @ 7.3%	0.95	0.91	0.91	0.89
Nuclear Fuel	1.30	0.80	0.90	0.50
Labor	0.08	0.08	0.08	0.08
Maintenance	0.08	0.08	0.08	0.08
Power	1.14	0.72	0.81	0.53
Total - ¢/lb. O_3	3.55	2.59	2.78	2.08

TABLE 12

CHEMONUCLEAR OZONE

INVESTMENT COST - MILLION DOLLARS

T - Capacity, Tons O_3/Day	40		40	
G - Values, Molecules/100 eV	10		15	
E - Energy Deposition Efficiency	0.20	0.35	0.20	0.35
P - Reactor Power, MW(t)	42.5	24.2	28.3	16.1
O_2 Plant	1.00	1.00	1.00	1.00
Refrigeration Equipment	0.43	0.25	0.30	0.17
Nuclear Reactor	4.25	4.25	4.25	4.25
Freon Plant	2.00	2.00	2.00	2.00
Compressors	0.23	0.13	0.13	0.10
Total	7.91	7.63	7.68	7.52

T - Capacity, Tons O_3/Day	100		100	
G - Values, Molecules/100 eV	10		15	
E - Energy Deposition Efficiency	0.20	0.35	0.20	0.35
P - Reactor Power, MW(t)				
O_2 Plant	2.00	2.00	2.00	2.00
Refrigeration Equipment	1.07	0.63	0.75	0.43
Nuclear Reactor	7.50	7.50	7.50	7.50
Freon Plant	4.00	4.00	4.00	4.00
Compressors	0.50	0.28	0.28	0.22
Total	15.07	14.41	14.53	14.15

T - Capacity, Tons O_3/Day	200		200	
G - Values, Molecules/100 eV	10		15	
E - Energy Deposition Efficiency	0.20	0.35	0.20	0.35
P - Reactor Power, MW(t)	212	121	142	80
Oxygen Plant	2.90	2.90	2.90	2.90
Refrigeration	2.14	1.26	1.50	0.86
Nuclear Reactor	11.60	11.60	11.60	11.60
Freon Plant	5.80	5.80	5.80	5.80
Compressors	0.90	0.50	0.50	0.40
Total	23.34	22.06	22.30	21.56

T - Capacity, Tons O_3/Day	400		400	
G - Values, Molecules/100 eV	10		15	
E - Energy Deposition Efficiency	0.20	0.35	0.20	0.35
P - Reactor Power, MW(t)	424	242	284	160
Oxygen Plant	3.50	3.50	3.50	3.50
Refrigeration	4.30	2.50	3.00	1.70
Reactor	17.40	17.40	17.40	17.40
Freon Plant	7.00	7.00	7.00	7.00
Compressors	1.60	0.83	0.83	0.70
	33.80	31.23	31.73	30.30

TABLE 13

ELECTRIC DISCHARGE PRODUCTION COST - ¢/LB OZONE

Capacity - Tons/Day	40		100		200		400	
Power - KWH/lb.	3.75	5.00	3.75	5.00	3.75	5.00	3.75	5.00
Depreciation @ 7.3%	1.72	2.19	1.58	2.03	1.47	1.90	1.36	1.78
Power Cost* @ 5 Mil/KWH	2.50	3.12	2.50	3.12	2.50	3.12	2.50	3.12
@ 6 Mil/KWH	3.00	3.75	3.00	3.75	3.00	3.75	3.00	3.75
Labor	0.25	0.25	0.13	0.13	0.08	0.08	0.04	0.04
Maintenance	0.05	0.05	0.05	0.05	0.04	0.04	0.04	0.04
Total Cost @ 5 Mil/KWH	4.52	5.61	4.26	5.33	4.09	5.14	3.94	4.98
@ 6 Mil/KWH	5.02	6.24	4.76	5.96	4.59	5.77	4.44	5.59

*Power Cost includes additional 1.25 KWH/Lb. for auxiliaries, as shown in Table 8.

TABLE 14

ELECTRIC DISCHARGE OZONE

INVESTMENT COSTS - MILLION DOLLARS

Capacity - Tons/Day	40		100		200		400	
Power Requirements	3.75	5.00	3.75	5.00	3.75	5.00	3.75	5.00
Ozonizers	2.62	3.49	5.97	7.97	11.20	14.90	20.90	27.90
Recycle Equipment	1.36	1.81	3.40	4.53	6.80	9.05	13.60	18.10
Construction	0.64	0.85	1.60	2.13	3.20	4.26	6.40	8.52
Oxygen Plant	1.00	1.00	2.00	2.00	2.90	2.90	3.50	3.50
Total	5.62	7.15	12.97	16.63	24.10	31.11	44.40	58.02

TABLE 15

CHEMONUCLEAR OZONE SYSTEM

POWER REQUIREMENTS - MW (e)

40 Tons/Day	G=10		G=15	
	E=0.20	0.35	E=0.20	0.35
O_2 Plant	0.7	0.7	0.7	0.7
Recycle Refrig.	3.0	1.7	2.0	1.1
Freon Plant	0.4	0.4	0.4	0.4
Compressors	3.5	2.0	2.3	1.3
	7.6	4.8	5.4	3.5

100 Tons/Day	10		15	
O_2 Plant	1.75	1.75	1.75	1.75
Refrig.	7.50	4.25	5.0	2.75
Freon Plant	1.0	1.0	1.0	1.0
Compressors	8.75	5.0	5.75	3.25
	19.00	12.00	13.50	8.75

200 Tons/Day	10		15	
O_2 Plant	3.5	3.5	3.5	3.5
Refrig.	15.0	8.5	10.0	5.5
Freon Plant	2.0	2.0	2.0	2.0
Compressors	17.5	10.0	11.5	6.5
	38.00	24.0	27.0	17.5

400 Tons/Day	10		15	
O_2 Plant	7.0	7.0	7.0	7.0
Refrig.	30.0	17.0	20.0	11.0
Freon Plant	4.0	4.0	4.0	4.0
Compressors	35.0	20.0	23.0	13.0
	76.0	48.0	54.0	35.0

TABLE 16

ELECTRIC DISCHARGE OZONE SYSTEM

POWER REQUIREMENTS - MW (e)

	Capacity - Tons/Day			
	40	100	200	400
Ozonizers @ 3.75 KWHR/lb.	12.5	31.3	62.5	125.0
Oxygen Plant	0.7	1.8	3.5	7.0
Auxiliaries	3.5	8.7	17.5	35.0
Total Power	16.7	41.8	83.5	167.0
Ozonizers @ 5.00 KWHR/lb.	16.7	41.7	83.5	167.0
Oxygen Plant	0.7	1.8	3.5	7.0
Auxiliaries	3.5	8.7	17.5	35.0
Total Power	20.9	52.2	104.5	209.0

TABLE 17

CHEMONUCLEAR OZONE

ENERGY REQUIREMENTS KWH/LB. O_3

	G=10, E=0.20	G=15, E=0.35
Reactor, Thermal	12.80	4.85
O_2 Plant, Electrical	0.21	0.21
Refrigeration, Electrical	0.95	0.33
Compressors, Electrical	1.05	0.39
Total Electrical	2.21	0.93

TABLE 18

ELECTRIC DISCHARGE OZONE

ENERGY REQUIREMENTS - KWH (ELECTRICAL)/LB. O_3

Electric Ozonizers	3.75	5.00
O_2 Plant	0.21	0.21
Auxiliaries	1.04	1.04
Total Electrical	5.00	6.25

2. Power cost--5 mils per kw-hr.

3. Gas refrigeration cost is $200 per ton.

4. 7.3% annual fixed charge rate on capital investment. This is mainly taken from the point of view of municipal water treatment plants.

5. Labor costs

   a. For the 200 and 400 ton/day plants, labor is 6 men per shift, 3 shifts, at $10,000 per man year.

   b. For the 40 and 100 ton/day plants, 5 men per shift, 3 shifts, at $10,000 per man year.

6. Maintenance cost equals labor cost for the 400 ton/day plant, and is scaled for the smaller plants by a 0.7 power factor of the plant capacity.

7. Compressor and refrigeration costs were obtained from commercial vendors, as were oxygen plant costs.

8. Reactor costs obtained from estimate by Burns & Roe and BNL based on G.E. and Westinghouse price books.

9. The Freon system was estimated at twice the cost of the oxygen plant because of additional columns and shielding.

Chemonuclear reactor power is derived from the equation:

$$P = \frac{101.5T}{GEM}$$

where

P is the reactor power, megawatts

T = ozone production, ton/day

G = G-value for ozone formation, molecules/100 eV

E = Energy absorption efficiency, a fraction

M = Molecular weight of product

Conventional Case - Electric Discharge Ozonizers

1. Costs of ozonizers obtained from Welsbach Bulletin 201;[32] also construction and recycle equipment costs; the larger capacity costs have been extrapolated using a 0.9 power factor.

2. 7.3% fixed charge rate on capital.

3. Labor cost is half that of chemonuclear case.

4. Maintenance cost is equal to labor cost for 400 ton/day plant, and scaled by 0.9 power factor for smaller plants.

The costs of the storage and distribution system were evaluated. These include Freon-11 absorber, truck fleet, storage tanks and refrigeration systems. A breakdown for a typical case of a 250,000 gal/day AMD plant with 200 ppm Fe^{+2}, and based on a 200 ton per day central plant, is shown in Table 19. The effect of varying ferrous iron content is shown below:

Fe^{+2} Content-ppm.	50	300	1000
Ozone Distribution Cost-¢/lb O_3	4.3	4.3	3.30
Ozone Distribution Cost-¢/1000 g/AMD	0.9	5.4	14.0

Maximum shipping distance is 75 miles; however, the costs are insensitive to the shipping distance within the Pennsylvania area.

Costs would not change much for larger AMD plants, although some savings could undoubtedly be achieved through optimization of the storage tank sizes and delivery schedules.

TABLE 19

STORAGE AND DISTRIBUTION COSTS

1. ADDITIONS REQUIRED TO 200 TON/DAY CENTRAL OZONE PLANT

Absorbers	$1,225,000
Storage Tank & Pumps	625,000
Refrigeration Unit	1,225,000
Total	3,075,000

$3,075,000 @ 7.3% Fixed Charge Rate = 0.18¢/lb O_3

2. ADDITIONS TO 250,000 GAL./DAY AMD PLANT (208 lb/day O_3)

Refrigeration Unit	$ 4,000
O_3 in F-11 Storage Tank	16,000
F-11 Return Tank	4,000
Total	24,000

$24,000 @ 7.3% Fixed Charge Rate = 3.0¢/lb O_3

3. FREON-11 INVESTMENT

3,350,000 lb @ 20¢/lb = $670,000 = 0.04¢/lb O_3

Losses = .0036 lb F-11/lb O_3 = 0.07¢/lb O_3

4. TRAILER FLEET

85 Tandem Axle Twin Screw Tractors, each with 5300 Gal. Vacuum Insulated Cryogenic Tank, @ $45,000 each = $3,825,000 (Includes 5 Spare Trucks) at 10 yr life, $382,000/yr

Labor - 80 Drivers, $10,000/yr = $800,000/yr

Total - $1,182,000/yr = 1.0¢/lb O_3

TOTAL SHIPPING AND DISTRIBUTION COST - 4.3¢/lb O_3

Comparisons of one-site ozone production costs with central plant generating and distribution costs show that the central plants can offer savings of as much as 10-34¢ per 1000 gal. AMD treated over the ranges of flow and concentration considered in this study. The greatest savings are at the high-flow, high Fe^{++} concentrations. The chemonuclear method shows savings of 1-7¢ per 1000 gal. AMD over the electric discharge method in the range of 40-200 tons/day ozone.

6.3 AMD TREATMENT PLANT

The investment costs for the AMD treatment plants at the mine sites are listed in Table 20. Operating costs are listed in Table 21, and do not include the cost of ozone. Labor is also excluded at this point since it is assumed that for on-site ozone generation, the operators from the ozone plant can perform the minimal operations required in the treatment plant. For the central plant cases, labor is not available from the ozone plant for the minimal operations required at the AMD treatment site. Therefore, a labor charge was added for these cases, amounting to 1 man-hr at $5 per hr for the 250,000 gal/day case, or 2¢ per 1000 gal. AMD. This charge is scaled down for the larger AMD treatment plants. These situations are summarized in Table 22-24, which give the total treatment costs, including ozone, for both the on-site and central ozone generating situations. These results are also shown graphically on Figures 20 through 22. Total investment costs for on-site electric discharge ozonizers and AMD treatment are shown in Table 25 and Figure 23.

Table 26 is a summation of the total treatment costs for purposes of comparison. It shows that for on-site ozone plants, recycled oxygen feed is preferable to once-through air feed, with the exception of the special case of low-flow, low Fe^{+2} streams. Central ozone plants with distribution systems offer lower costs than on-site plants, particularly for high Fe^{+2} and flow situations. Central chemonuclear plants result in lower costs than electric discharge facilities. Treatment cost ranges, from Table 26, are seen to be from 9-13¢ per 1000 gal. at 50 ppm Fe^{+2} over the flow range of 250,000 to 6,000,000 gal. per day. For higher Fe^{+2} concentrations, the treatment costs are 18-34¢ at 300 ppm, and 40-78¢ at 1000 ppm Fe^{+2} over the same AMD flow range.

Central chemonuclear ozone plants with distribution systems and high AMD flow rates offer the lowest costs in the above ranges. The highest cost is for on-site electric discharge ozone at low flow rates. An interesting elaboration can be made here regarding central

TABLE 20

AMD PLANT COST IN THOUSANDS OF DOLLARS

Case	AMD Flow gal/day	Fe^{+2} conc. ppm	Oxidation vessels	Agitators	Limestone mill	Piping & neutr T	Misc., Instr.& control	Holding pond	Settling pond	Total equipM&L) indirects	Total cost	¢/1000 gal.
1	6×10^6	1000	545	45	39	6	6	24	48	713	855	3.6
2	"	300	545	45	20	6	6	24	48	694	830	3.4
3	"	50	545	45	9	6	6	24	24	659	790	3.2
4	1×10^6	1000	102	9	16	4	3	4	8	146	175	4.3
5	"	300	102	9	6	4	3	4	5	136	163	4.0
6	"	50	102	9	4	4	3	4	4	130	156	3.8
7	$\frac{1}{4} \times 10^6$	1000	29	3	4	3	1	1	3	44	53	5.2
8	"	300	29	3	4	3	1	1	3	44	53	5.2
9	"	50	29	3	4	3	1	1	2	43	52	5.1

TABLE 21

AMD TREATMENT PLANT OPERATING COSTS* - ¢/1000 GAL.

AMD Flow Gal./Day	0.25×10^6			1×10^6			6×10^6		
Fe^{++}, ppm.	50	300	1000	50	300	1000	50	300	1000
Depreciation @ 7.3%	5.1	5.2	5.2	3.8	4.0	4.3	3.2	3.4	3.6
Power @ 8 mil.Kw-Hr	3.2	3.3	3.5	3.2	3.3	3.5	3.2	3.3	3.5
Limestone @ $5/Ton	0.5	1.6	4.4	0.5	1.6	4.4	0.5	1.6	4.4
TOTAL	8.8	10.1	13.1	7.5	8.9	12.2	6.9	8.3	11.5

*Not including ozone.

TABLE 22

AMD TREATMENT TOTAL OPERATING COST

¢/1000 Gal.

AMD FLOW, GPD	0.25×10^6			1.0×10^6			6.0×10^6		
Fe^{++}, ppm	50	300	1000	50	300	1000	50	300	1000
OZONE GENERATED ON SITE-ELECTRIC DISCHARGE OZONIZERS									
A. ONCE-THROUGH AIR FEED, 7.25 KW-Hr/lb									
OZONE	3.6	20.1	61.1	3.4	18.1	55.0	2.8	16.0	51.7
AMD PLANT	8.8	10.1	13.1	7.5	8.9	12.2	6.9	8.3	11.5
TOTAL	12.4	30.2	74.3	10.9	27.0	67.2	9.7	24.3	63.2
B. ONCE-THROUGH AIR FEED, 9.75 KW-Hr/lb									
OZONE	4.2	24.8	75.3	4.2	22.2	67.9	3.7	19.6	62.5
AMD PLANT	8.8	10.1	13.1	7.5	8.9	12.2	6.9	8.3	11.5
TOTAL	13.0	34.9	88.4	11.7	31.1	80.1	10.6	27.9	74.0
C. OXYGEN FEED WITH RECYCLE, 3.75 KW-Hr/lb									
OZONE	4.9	21.2	56.5	3.7	16.5	45.7	2.7	12.6	35.8
AMD PLANT	8.8	10.1	13.1	7.5	8.9	12.2	6.9	8.3	11.5
TOTAL	13.7	31.3	69.6	11.2	25.4	57.9	9.6	20.9	47.3
D. OXYGEN FEED WITH RECYCLE, 5.0 KW-Hr/lb									
OZONE	5.5	24.1	65.2	4.3	19.1	52.9	3.2	14.5	42.1
AMD PLANT	8.8	10.1	13.1	7.5	8.9	12.2	6.9	8.3	11.5
TOTAL	14.3	34.2	78.3	11.8	28.0	65.1	10.1	22.8	53.6

TABLE 23

OZONE GENERATED IN 40 TON/DAY CENTRAL PLANT, SHIPPED TO AMD SITE

¢/1000 Gal.

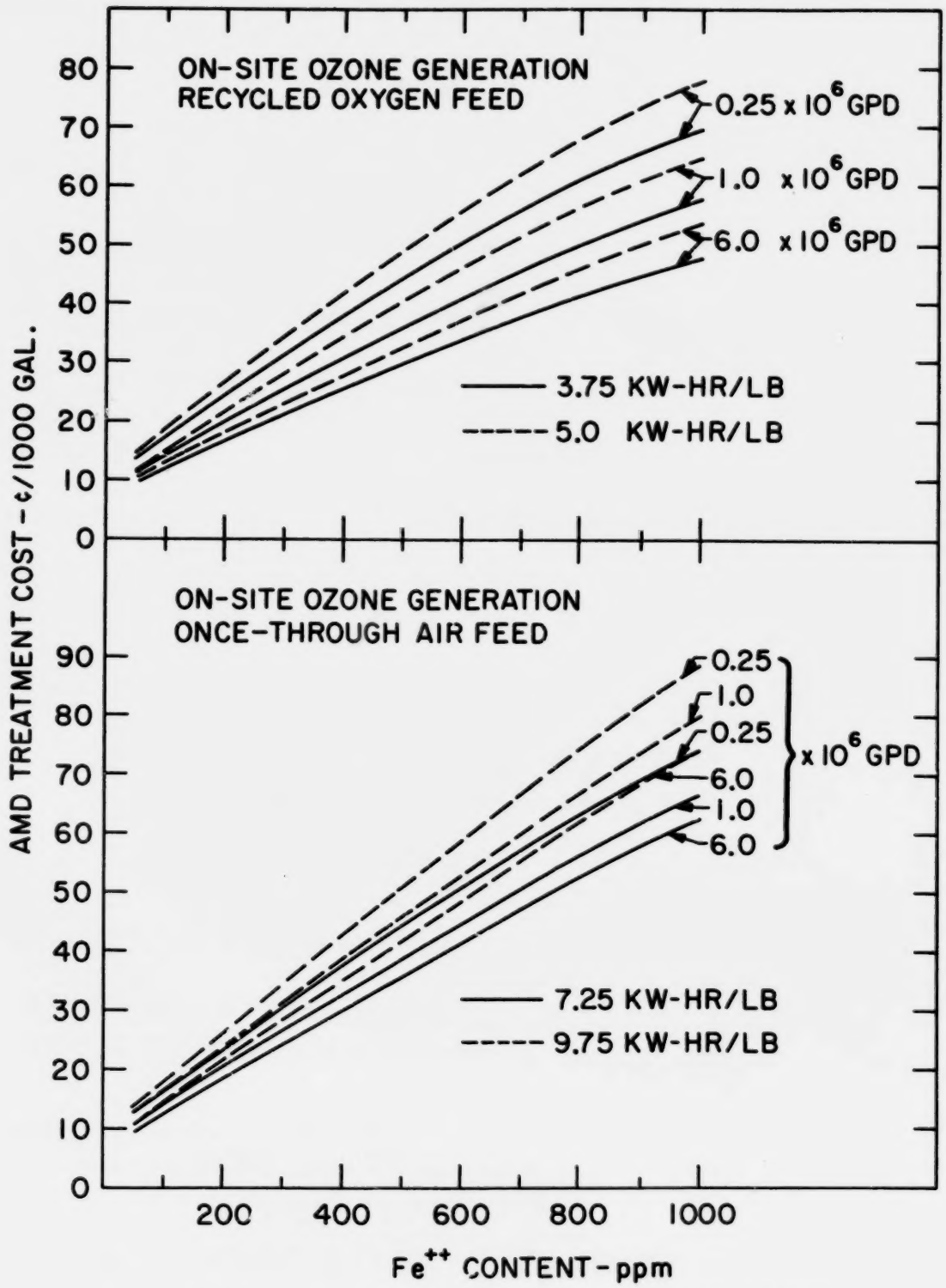
AMD FLOW, GPD	0.25 X 10^6			1.0 X 10^6			6.0 X 10^6		
Fe^{++}, ppm	50	300	1000	50	300	1000	50	300	1000
A. ELECTRIC DISCHARGE OZONIZERS, RECYCLED O_2, 5 KW-Hr/lb									
1. 5 MIL./KW-Hr POWER COST									
OZONE	1.2	7.0	23.3	1.2	7.0	23.3	1.2	7.0	23.3
AMD PLANT	8.8	10.1	13.1	7.5	8.9	12.2	6.9	8.3	11.5
DISTRIBUTION	0.9	5.4	14.0	0.9	5.4	14.0	0.9	5.4	14.0
LABOR	2.0	2.0	2.0	1.0	1.0	1.0	0.5	0.5	0.5
TOTAL	12.9	24.5	52.4	10.6	22.3	50.5	9.5	21.2	49.3
2. 6 MIL./KW-Hr POWER COST									
OZONE	1.5	8.0	26.0	1.5	8.0	26.0	1.5	8.0	26.0
AMD PLANT	8.8	10.1	13.1	7.5	8.9	12.2	6.9	8.3	11.5
DISTRIBUTION	0.9	5.4	14.0	0.9	5.4	14.0	0.9	5.4	14.0
LABOR	2.0	2.0	2.0	1.0	1.0	1.0	0.5	0.5	0.5
TOTAL	13.2	25.5	55.1	10.9	23.3	53.2	9.8	22.2	52.0
B. CHEMONUCLEAR OZONE, RECYCLED O_2									
1. G = 15, E = 0.20									
OZONE	1.0	5.8	19.5	1.0	5.8	19.5	1.0	5.8	19.5
AMD PLANT	8.8	10.1	13.1	7.5	8.9	12.2	6.9	8.3	11.5
DISTRIBUTION	0.9	5.4	14.0	0.9	5.4	14.0	0.9	5.4	14.0
LABOR	2.0	2.0	2.0	1.0	1.0	1.0	0.5	0.5	0.5
TOTAL	12.7	23.3	48.6	10.4	21.1	46.7	9.3	20.0	45.5
2. G = 10, E = 0.20									
OZONE	1.3	6.8	22.5	1.3	6.8	22.5	1.3	6.8	22.5
AMD PLANT	8.8	10.1	13.1	7.5	8.9	12.2	6.9	8.3	11.5
DISTRIBUTION	0.9	5.4	14.0	0.9	5.4	14.0	0.9	5.4	14.0
LABOR	2.0	2.0	2.0	1.0	1.0	1.0	0.5	0.5	0.5
TOTAL	13.0	24.3	51.6	10.7	22.1	49.7	9.6	21.0	48.5

TABLE 24

OZONE GENERATED IN 200 TON/DAY CENTRAL PLANT, SHIPPED TO AMD SITE

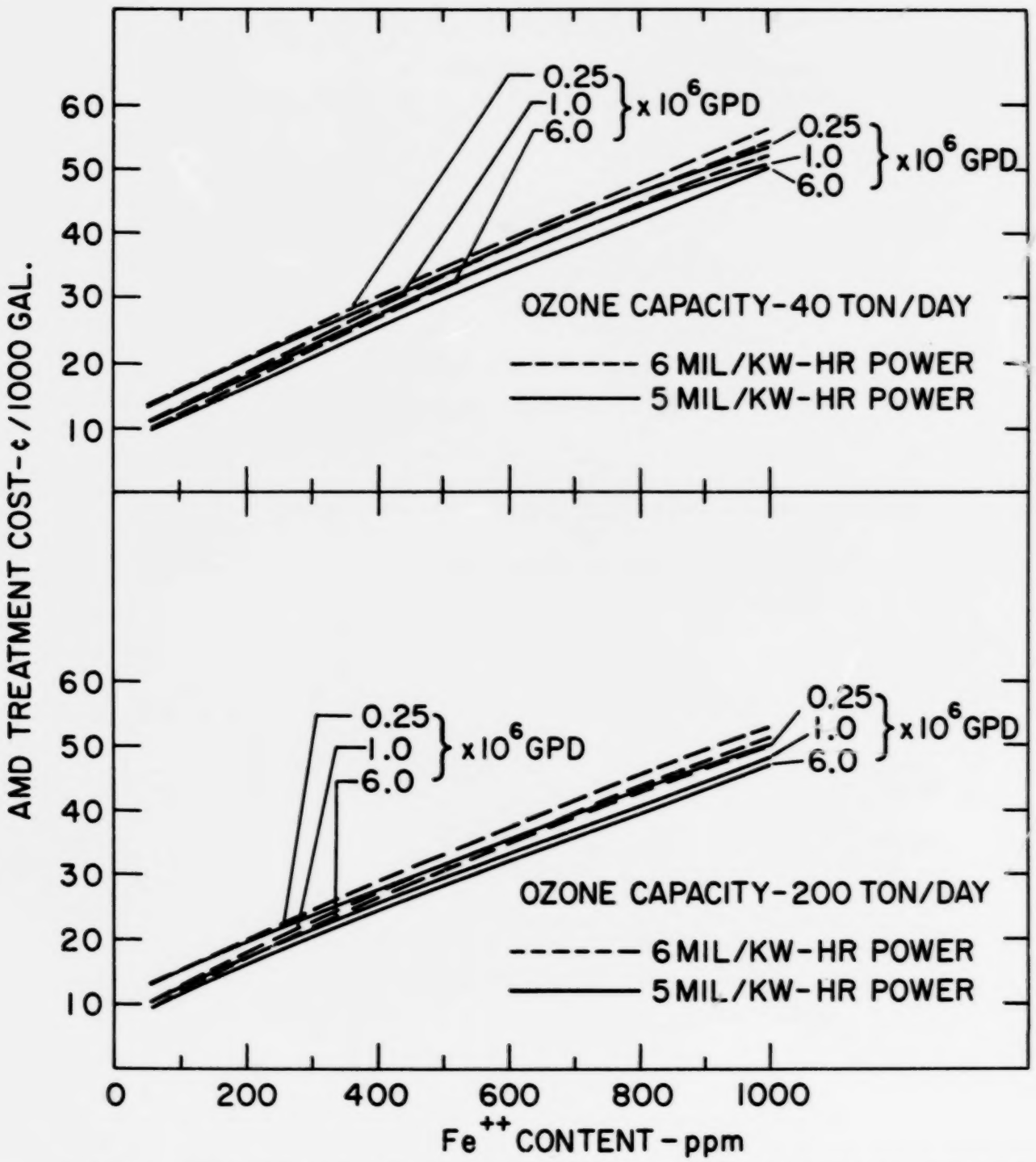
¢/1000 Gal.

AMD FLOW, GPD	0.25×10^6			1.0×10^6			6.0×10^6		
Fe^{++}, ppm	50	300	1000	50	300	1000	50	300	1000
A. ELECTRIC DISCHARGE OZONIZERS, RECYCLED O_2, 5 KW-Hr/lb									
1. 5 MIL./KW-HR POWER COST									
OZONE	1.1	6.4	21.3	1.1	6.4	21.3	1.1	6.4	21.3
AMD PLANT	8.8	10.1	13.1	7.5	8.9	12.2	6.9	8.3	11.5
DISTRIBUTION	0.9	5.4	14.0	0.9	5.4	14.0	0.9	5.4	14.0
LABOR	2.0	2.0	2.0	1.0	1.0	1.0	0.5	0.5	0.5
TOTAL	12.8	23.9	50.4	10.5	21.7	48.5	9.4	20.6	47.3
2. 6 MIL./KW-HR POWER COST									
OZONE	1.2	7.2	24.0	1.2	7.2	24.0	1.2	7.2	24.0
AMD PLANT	8.8	10.1	13.1	7.5	8.9	12.2	6.9	8.3	11.5
DISTRIBUTION	0.9	5.4	14.0	0.9	5.4	14.0	0.9	5.4	14.0
LABOR	2.0	2.0	2.0	1.0	1.0	1.0	0.5	0.5	0.5
TOTAL	12.9	24.7	53.1	10.6	22.5	51.2	9.5	21.4	50.0
B. CHEMONUCLEAR OZONE, RECYCLED O_2									
1. G = 15, E = 0.20									
OZONE	0.7	4.1	13.7	0.7	4.1	13.7	0.7	4.1	13.7
AMD PLANT	8.8	10.1	13.1	7.5	8.9	12.2	6.9	8.3	11.5
DISTRIBUTION	0.9	5.4	14.0	0.9	5.4	14.0	0.9	5.4	14.0
LABOR	2.0	2.0	2.0	1.0	1.0	1.0	0.5	0.5	0.5
TOTAL	12.4	21.6	42.8	10.1	19.4	40.9	9.0	18.3	39.7
2. G = 10, E = 0.20									
OZONE	0.9	5.2	17.3	0.9	5.2	17.3	0.9	5.2	17.3
AMD PLANT	8.8	10.1	13.1	7.5	8.9	12.2	6.9	8.3	11.5
DISTRIBUTION	0.9	5.4	14.0	0.9	5.4	14.0	0.9	5.4	14.0
LABOR	2.0	2.0	2.0	1.0	1.0	1.0	0.5	0.5	0.5
TOTAL	12.6	22.7	46.4	10.3	20.5	44.5	9.2	19.4	43.3



TOTAL AMD TREATMENT COSTS USING OZONE
ELECTRIC DISCHARGE OZONIZERS

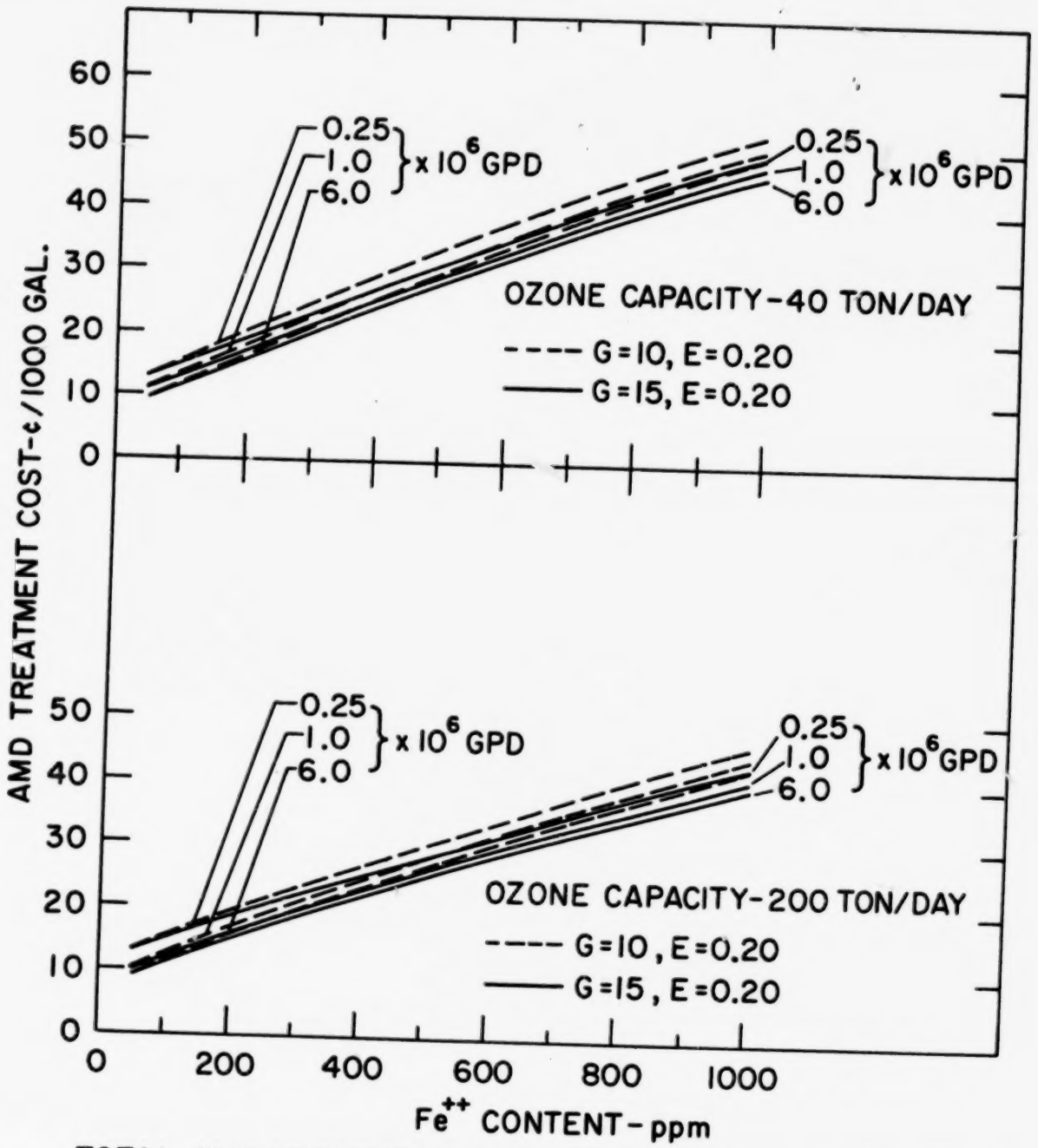
FIGURE 20



TOTAL AMD TREATMENT COST USING ELECTRIC-DISCHARGE OZONE

CENTRAL PLANT OZONE GENERATION, SHIPPED TO AMD SITE
5 KW-HR/LB O_3 POWER CONSUMPTION

FIGURE 21



TOTAL AMD TREATMENT COST USING CHEMONUCLEAR OZONE CENTRAL PLANT OZONE GENERATION, SHIPPED TO AMD SITE

FIGURE 22

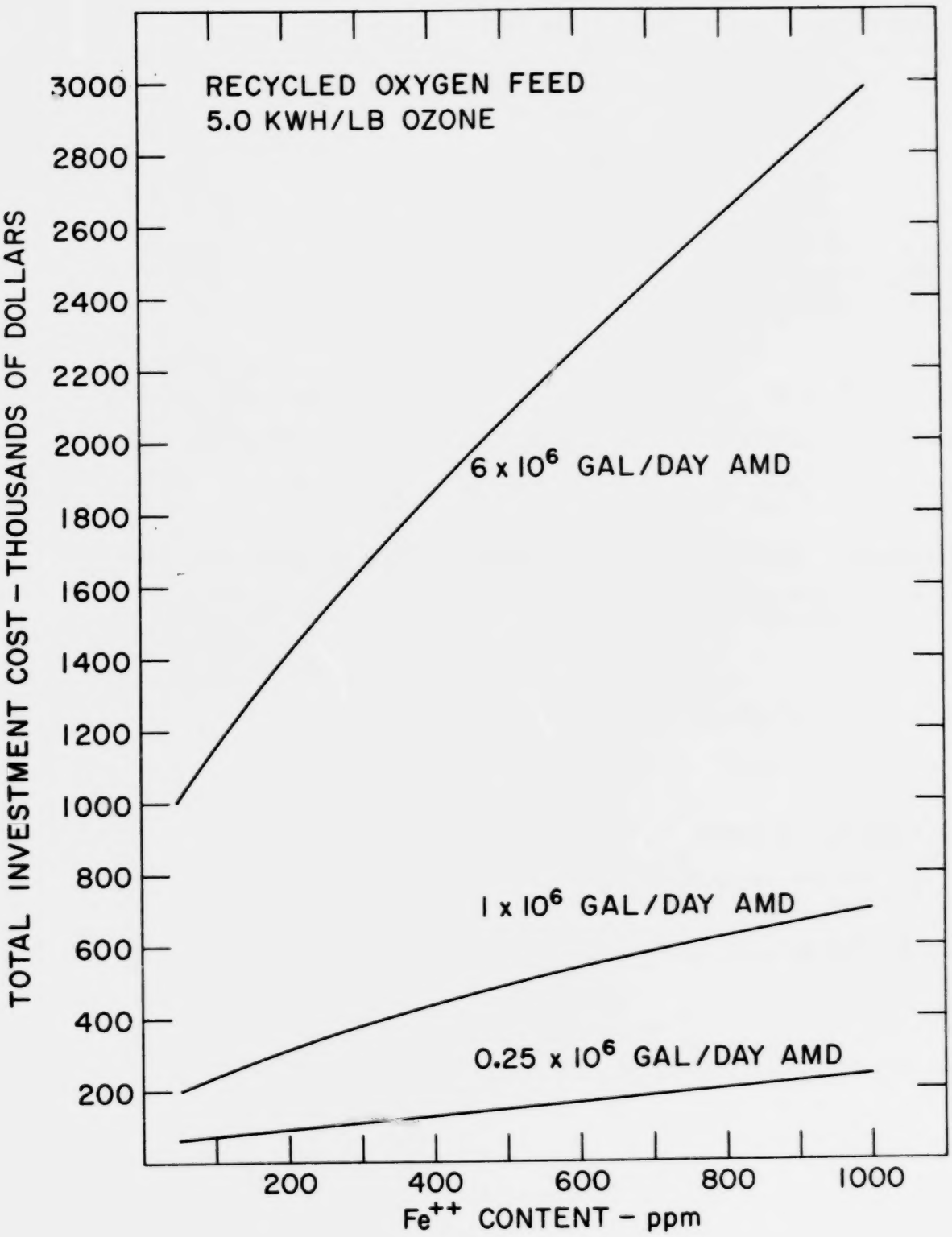
TABLE 25

TOTAL INVESTMENT COSTS FOR AMD TREATMENT
USING ON-SITE OZONE WITH RECYCLED OXYGEN FEED

5.0 KWH/LB OZONE

COSTS IN THOUSANDS OF DOLLARS

AMD FLOW, GAL./DAY	250,000			1,000,000			6,000,000		
Fe^{+2} CONC'N ppm	50	300	1000	50	300	1000	50	300	1000
OZONE PLANT	14	60	190	40	220	530	220	810	2130
AMD PLANT	52	53	53	156	163	175	790	830	855
TOTAL $	66	113	243	196	383	705	1010	1640	2985



TOTAL PLANT INVESTMENT COST FOR AMD TREATMENT
USING ON-SITE ELECTRIC DISCHARGE OZONE

FIGURE 23

TABLE 26

COMPARISON OF AMD TOTAL TREATMENT COSTS

COSTS IN CENTS PER 1000 GAL.

AMD FLOW - GAL. PER DAY

	0.25×10^6			1.0×10^6			6.0×10^6		
Fe^{++} CONTENT-ppm	50	300	1000	50	300	1000	50	300	1000
1. ELECTRIC DISCHARGE WITH RECYCLED OXYGEN FEED, ON-SITE OZONE GENERATION									
@ 3.75 Kwh/lb.	14	31	70	11	25	58	10	21	47
@ 5.00 Kwh/lb.	14	34	78	12	28	65	10	23	54
2. ELECTRIC DISCHARGE WITH ONCE-THROUGH AIR FEED, ON SITE OZONE GENERATION									
@ 7.25 Kwh/lb.	12	30	74	11	27	67	10	24	63
@ 9.25 Kwh/lb.	13	35	88	12	31	80	11	28	74
CENTRAL OZONE PLANTS WITH DISTRIBUTION SYSTEMS									
3. ELECTRIC DISCHARGE, 40 TON/DAY OZONE									
@ 5 mil/Kwh power	13	24	52	11	22	50	10	21	49
@ 6 mil " "	13	26	55	11	23	53	10	22	52
4. ELECTRIC DISCHARGE, 200 TON/DAY OZONE									
@ 5 mil/Kwh power	13	24	50	10	22	48	9	21	47
@ 6 mil/ " "	13	25	53	11	23	51	9	21	50
5. CHEMONUCLEAR, 40 TON/DAY OZONE									
G=10, E=0.20	13	24	52	11	22	50	10	21	48
G=15, E=0.20	13	23	49	10	21	47	9	20	45
6. CHEMONUCLEAR, 200 TON/DAY OZONE									
G=10, E=0.20	13	23	46	10	21	44	9	19	43
G=15, E=0.20	12	22	43	10	19	41	9	18	40

plants. One might wish to ascertain the over-all desirability of building central ozone generating facilities, considering both the investment and operating costs. Taking the southwest Pennsylvania situation of 486,000,000 gal./day AMD flow, at an average Fe^{+2} concentration of about 200 ppm, the total investment cost necessary for central ozone plants, both chemonuclear and electric discharge, was calculated. The investment in AMD neutralization facilities at the 2,160 sites was also calculated, and these are compared with on-site ozone generation (via electric discharge) and AMD neutralization, as shown in Table 27. Operating costs for these situations are also included in the breakdown. It is seen that both investment and operating costs are lower for central plants, whether they utilize chemonuclear or electric discharge ozone. Note that the investment cost for the central ozone generating plants include an oxygen plant and the necessary storage and distribution equipment for ozone shipment. The AMD neutralization facilities at each site utilizing shipped ozone also include storage equipment in their investment cost. The on-site plant cost consists of $52,000 for neutralization equipment and $20,000 for ozone storage. The total over-all investment and operating costs may be considered on the high side for this situation because, in actuality, many AMD sites would have higher flows than this average case. As a result, investment and operating costs would both be lower. The main purpose of presenting this data is merely to indicate the magnitude of the costs involved and the relative merits of each system.

Since the chemonuclear system is not a fully developed process, the additional development cost of the process should be considered. Possibly five years of development at a cost of $10-$15,000,000 might be required to bring this process to the point which would permit construction of the 200-ton per day central plant. In this light, the first cost of chemonuclear vs. electric discharge ozone would be roughly equivalent. However, the operating costs for the chemonuclear case are lower than those for electric discharge; reference to Table 27 shows the chemonuclear operating cost to be 2¢ per 1000 gal. lower than electric discharge.

TABLE 27

COST BREAKDOWN FOR TOTAL AMD TREATMENT OF PENNSYLVANIA AMD STREAMS

486 MILLION GALLONS PER DAY

Investment Costs - Million Dollars

	Central Chemo-nuclear	Central Elec. Disch.	On-Site Elec. Disch.
Ozone Plants	26.0	34.8	99.5
AMD Neutralization*	156.0	156.0	113.0
Total Investment	182.0	190.8	212.5

Operating Costs - ¢/1000 Gal.

	Central Chemo-nuclear	Central Elec. Disch.	On-Site Elec. Disch.
Depreciation-7.3%	9.1	9.6	10.6
Nucl. Fuel Cycle	0.9	-	-
Labor	2.1	2.1	1.0
Power	3.9	6.3	7.2
Maintenance	0.1	0.1	1.0
Purchased Oxygen	-	-	5.4
Distribution	0.8	0.8	-
Limestone	1.2	1.2	1.2
Total Operating Costs	18.1	20.1	26.4
Annual Operating Costs	$\$26.4 \times 10^6$	$\$29.3 \times 10^6$	$\$38.5 \times 10^6$

*Assumes 2,160 AMD treatment sites with average flow rates of 250,000 gpd.

6.4 COMPARISON WITH PRESENT METHODS

Comparison of the ozone oxidation and neutralization method with presently used methods is difficult and hazardous, since a common basis for comparison should be used, but does not exist. In particular, one reason is that the coal industry uses costs based on a per ton of coal mined depreciation method; this in itself means that each mine is capitalized differently. However, Martin and Hill[3] of FWQA state costs of neutralization can vary from 10¢ to $1.30 per thousand gal. AMD. The present study shows costs ranging from 9-78¢ maximum; thus, on this basis, ozone treatment is not out of line.

At the Third AMD Symposium in Pittsburgh, it was stated[35] that a 1-million gal. per day AMD plant, treating 150 ppm Fe^{++}, could be built for an equipment cost of $350,000. Using the same fixed charge rate (7.3%) as this study, and adding appropriate lime, labor and power costs, the AMD treatment cost for that situation is estimated to be in the 17¢ per 1000 gal. range, as illustrated in Table 28. The estimate for ozone treatment cost for the same case is 16¢ per 1000 gal. using on-site electric discharge ozone and limestone treatment, and a total investment cost of $280,000. Using ozone obtained from a chemonuclear central plant, the treatment cost would be lowered to 13¢ per 1000 gal., at an investment cost of $184,000. This infers that the use of ozone permits operation at lower costs than those presently attained. The reason is that the costs of ozone generation equipment are of approximately the same magnitude as the clarifier-thickeners presently used, which are large, costly pieces of equipment. Also, the ozone process offers the benefit of permitting the use of limestone, at $5 per ton, over lime which costs $17-$18 per ton.

TABLE 28

COST OF CONVENTIONAL AMD TREATMENT

BASIS: 1 MILLION GAL./DAY AMD

Fe^{+2} CONTENT = 150 ppm.

INVESTMENT = $350,000

@ 7.3% FIXED CHARGE RATE = 8.6¢/1000 GAL.

OPERATING COST	¢/1000 GAL.
DEPRECIATION	8.6
LIME @$18/TON	4.2
POWER	3.3
LABOR	1.0
TOTAL	17.1¢/1000 GAL.

7. DISCUSSION

The benefits of ozone usage are seen as follows. Ozone permits rapid and efficient oxidation of Fe^{+2} in acid media. Process control becomes much simpler, because the close control required in the present process, which uses lime, is not required. Because the oxidation can proceed at low pH, neutralization can stop at pH 7, thus reducing limestone requirements and sludge handling, whereas at present the pH must be brought above 8.0 for effective oxidation using air. The high reactivity of ozone results in a higher oxidation rate, increasing the throughput available for a given investment, and decreasing the investment required for land for holdup ponds. Limestone also results in higher sludge density and faster settling times; this again reduces settling pond requirements, fluid handling equipment, and ultimate disposal problems.

The problem of sludge disposal cannot be covered here, since each AMD site has its own peculiarities. Some sites have worked out mines and bore-holes available for sludge disposal, and others require that the sludge be pumped over relatively large distances for disposal. In some cases, the sludge is actually trucked to a disposal point. Therefore, it is impossible to speculate about disposal costs. However, the anticipated higher sludge density and lower water content of the sludge should result in an appreciable cost reduction for disposal.

As a result of this study, which shows favorable economic feasibility, it is recommended that the proposal[36] originally submitted to the Commonwealth of Pennsylvania Bureau of Mines and FWQA for "Treatment of Acid Mine Drainage by Ozone Oxidation," which called for a mobile demonstration plant to evaluate the field practicability of the process, be constructed and operated. This would permit obtaining the required data on oxidation rates, sludge density and settling rates, and actual operating costs. Although chemonuclear ozone is more economical in the long term, the

demonstration system should employ electric-discharge ozone because the small unit required is readily available. The investigation of new and improved methods of ozone production should also be pursued.

Based on the results of the field study, a firm decision could be made regarding the potential benefits of ozone treatment. It may then be desirable to enter into a small development program for central plant ozone production and shipping, which offers distinct economic advantages for high-flow, high iron AMD streams.

ACKNOWLEDGEMENT

The authors of this report are:

M. Beller
C. Waide
M. Steinberg
Department of Applied Science
Brookhaven National Laboratory
Upton, New York 11973

The authors acknowledge the contribution of Dr. J.R. Powell for Appendix A on the Electric Field-Radiation Ozonizer, and also the review and suggestions made by Mr. B. Manowitz of the Department of Applied Science, Brookhaven National Laboratory, and Dr. J.M. Shackelford of the Environmental Protection Agency.

REFERENCES

1. E. A. Zawadzki, Acid Mine Drainage Research at Bituminus Coal Research, Inc. Presented at AIME Meeting, Las Vegas, Nevada, (September 8, 1967).

2. States Make Headway on Mine Drainage, Environmental Science and Technology, Vol. 3, No. 12, 1237-9, (December 1969).

3. Second Symposium on Coal Mine Drainage Research, Sponsored by the Ohio River Valley Water Sanitation Commission, Pittsburgh, Pa., (May 1968).

4. Third Symposium on Coal Mine Drainage Research, Sponsored by the Ohio River Valley Water Sanitation Commission, Pittsburgh, Pa., (May 19-20, 1970).

5. W. Stumm, G. F. Lee, Ind. Eng. Chem., Vol. 53, No. 2, p. 143-6 (February 1961).

6. R. B. Rozelle, et al, Studies on the Removal of Iron from Acid Mine Drainage Water, Wilkes College Research and Graduate Center. Submitted to Coal Research Board, Commonwealth of Pennsylvania, (June 1968).

7. E. A. Mihok, M. Deuhl, C. E. Chamberlain and J. G. Selmeczi, Mine Water Research: The Limestone Neutralization Process, Report of Investigations, U. S. Bureau of Mines, Department of the Interior.

8. S. Sideman, O. Hortascsu and J. W. Fulton, Mass Transfer in Gas-Liquid Contacting Systems, Ind. & Eng. Chem. 58, No. 7, p. 32-47, (July 1966).

9. R. H. Perry, C. H. Chilton and S. D. Kirkpatrick, Chemical Engineers Handbook, Section 18, McGraw Hill, (1963).

10. F. Yoshida, A. Ikeda, S. Imakawa and Y. Miura, Oxygen Absorption Rates in Stirred Gas-Liquid Contractors, Ind. Eng. Chem. 52, No. 5, 435-438, (May 1960).

11. M. Steinberg, J. Pruzansky, L. R. Jefferson and B. Manowitz, Removal of Iron from Mine Drainage Waste with the Aid of High-Energy Radiation, Part I, Brookhaven National Laboratory Report No. 11576, (July 1967); Part II, BNL No. 12114, (Dec. 1967); Part III, BNL No. 12115, (Jan. 1968).

12. Matheson Gas Data Book, 4th Ed., The Matheson Co., Inc. (1966).

13. S. C. Lind, Radiation Chemistry of Gases, 83-86, Reinhold, New York, (1961).

14. D. W. Wall and L. A. Brown, J. Phys. Chem. 65, 915-919 (1961).

15. J. F. Kircher, J. S. McNutley, J. L. McFarling and A. Levy, Radiation Research 13, 452-65, (1960).

16. G. R. A. Johnson and J. M. Warman, Discussions, Faraday Society, 37, 87-95, (1964).

17. J. T. Sears and J. W. Sutherland, Nuclear Applications 2, 62-3, (1968).

18. Z. I. Kertesz and G. F. Parsons, Science 142, 1289-90, (1963).

19. L. N. Less and A. J. Swallow, Nucleonics 22, No. 9, 58-61, (1964).

20. J. Shah and E. C. Maxie, Intern. J. Appl. Radiation Isotopes, 17, 155-9, (1966).

21. M. Steinberg, "O_3 and NO_2 Formation by Irradiation of a N_2-O_2 Gas Mixture in a Flowing System at Elevated Pressures," BNL 50017, Brookhaven National Laboratory, Upton, N.Y., (Sept. 1966).

22. R. N. Dietz, J. D. Smith, M. Steinberg, (to be presented at Am. Chem. Soc. Meeting, New York, September 7-12, 1969).

23. J. A. Ghormley, C. J. Hochanadel and J. W. Boyle, J. Chem. Phys. 50, 419-23, (1969).

24. M. Steinberg, W. D. Tucker, C. Waide, M. Beller, P. Bezler, and B. Manowitz, "Safety Review of the Brookhaven Chemonuclear In-Pile Research Loop," BNL 13001, Brookhaven National Laboratory, Upton, N.Y. (Oct. 1968).

25. M. Steinberg, W. D. Tucker and G. Farber, Fission Fragment Recoil Energy Source and Chemonuclear Fuel Element, Am. Nucl. Soc. Trans. 10, 44, (June 1967).

26. M. Steinberg, Chem. Eng. Progress 62, No. 9, 195-16, (1966).

27. M. Beller, Internal Reports, Brookhaven National Laboratory, (Dec. 1968 - May 1969).

28. J. T. Sears and J. W. Sutherland, J. Phys. Chem. 72, 1166-71, (1968).

29. M. Steinberg, "The Recovery of Fission Product Xenon and Krypton by Absorption Processes," Brookhaven National Laboratory, BNL 542 (Jan. 1959).

30. J. R. Merriman, et al., "Concentration and Collection of Krypton and Xenon by Selective Absorption in Fluorocarbon Solvents," SM-110/25 (K-L-6198), Intl. Atomic Energy Agency Conference at Harvard University, Cambridge, Mass. (Aug. 1968).

31. Kirk-Othmer, "Encyclopedia of Chemical Technology," Vol. 14, 410-32, 2nd Ed., Interscience Publishers, (1967).

32. Technical Bulletin No.201, Welsbach Corp., Philadelphia, Pa., (1968).

33. C. McGuire, The Linde Co., Div. Union Carbide, Private Communication (June 1970).

34. R. A. Tybout, "A Cost-Benefit Analysis of Mine Drainage," Second Symposium of Coal Mine Drainage Research, Pittsburgh, Pa., (1968).

35. G. F. Haines, Jr., Personal Communication, (May 19, 1970).

36. Proposal on Treatment of Acid Mine Drainage by Ozone Oxidation, Brookhaven National Laboratory, Upton, N.Y., submitted to the Commonwealth of Pennsylvania Bureau of Mines and the FWQA (Nov. 1968, Rev. Feb. 1969).

37. Operation Yellowboy, Dow-Oliver, Inc., Stamford, Conn., (June 1966).

38. Oxygenation of Ferrous Iron, Harvard University, FWQA Report No. 14010, (June 1970).

39. Studies on Limestone Treatment of Acid Mine Drainage, Bitum. Coal Res., Inc., FWQA Report No. DAST-33, 14010 EIZ (Jan. 1970).

40. R. D. Hill and R. C. Wilmoth, Limestone Treatment of Acid Mine Drainage, FWQA Report No. 14010 (Oct. 1970).

APPENDIX A

The Combined Electric Field-Radiation Ozonizer

Conventional ozonizers have low chemical efficiency (8%) and low power density (~0.03 W/cm^3 at 60 cps). Further, they must operate with a small discharge gap (2 to 4 mm). The low power density and small gap cause a very high capital cost for the ozonizer. For example, a 600-ton/day ozone plant would require almost 30 million square feet of ozonizer surface (at 60 cps). This could be reduced by almost a factor of 100 by operating to higher frequencies (6000 cps), but a tremendous area would still be required. At 6000 cps, a 600-ton/day plant would require ~60 miles of 4-in.-diam ozonizers. (The discharge area varies inversely as frequency, but the discharge gap remains fixed.) Such a plant is impractically large.

The low power density and small gap of the conventional ozonizer are the result of the requirement that electrons in the gap be created by the electric field. To prevent arcing, a high resistance barrier (e.g., glass) is placed between the electrodes. This acts like a large resistance in series with the capacitance of the electrodes, and quenches the discharge. Considerable electrical energy is dissipated in the glass, lowering the efficiency. The power density is kept low since the charge produced in the corona streamer from the instantaneous cathode takes some time to leak through the glass, and a new streamer cannot be established until it does. The chemical efficiency of the ozonizer decreases with increasing gap, because the discharge tends to be more localized, with coarse, hot sparks. With very small gaps, the discharge is finer and more uniform. Ozone tends to be destroyed in hot spark channels. For example, for gaps of 0 to 2 mm, the ozone yield is ~200 g/kWh, but drop to ~100 g/kWh for gaps of 3 to 4 mm. Thus, though higher frequencies can increase power density, the discharge gap must remain fixed.

If the ionization process were independent of the electric field, ozonizers could operate with higher

efficiency, greater power density, and larger discharge gaps. The glass barrier in the ozonizer would no longer be necessary, since there would be no possibility of breakdown and arcing.

Radiation can provide ionization independent of the electric field. The radiation power would be a small fraction (e.g., 0.01 to 0.1%) of the electric field power, so the cost of the radiation would be low. This permits an electrochemical discharge that has much greater versatility than the conventional corona discharge (ozonizer), with a number of significant advantages:

1. The electron concentration and discharge power are controlled by the radiation intensity.

2. The discharge is spatially uniform, with no tendency to arc.

3. Discharge power can be much greater than that of a conventional discharge.

4. The electron energy in the conventional corona discharge is set by the condition that it be sufficient to generate additional electrons by electron-molecular conditions. This energy may not be the most favorable one for a given chemical reaction. In the electrochmical discharge, since the electrons are not produced by the electric field, the electron energy can be much less than it is in the corona discharge, and in fact, can be controlled by electric field strength. Thus, optimum electron energy can be selected for any process.

5. The time scale of the discharge can be controlled by the radiation source; that is, a short pulse of radiation could cause a very fast discharge. The radiation is then shut off, and the radicals produced react. This type of discharge may be more efficient than a continuous discharge.

The electrochemical discharge proposed here is a new type of chemical process. It has many other possible uses besides ozone production, for example, it may be

useful for NO synthesis, hydrazine production from ammonia, coal hydrogenation, acetylene production, and various organic reactions which cannot be carried out in a conventional corona discharge.

The electrochemical discharge can work at dc, low frequency, or high frequency. At dc or low frequency it is significantly better than the ozonizer but space charge effects limit its power density (~1 W/cm^3) and discharge gap (~10 mm). At high frequency, much larger discharge gaps and power densities are possible.

Researchers have worked with radiofrequency ozonizers and found very low chemical efficiencies (1% of conventional ozonizers). However, the condition that the electric field generates the electrons is the cause of this low efficiency. The ion density is so high that the plasma simply polarizes with a large part of the applied voltage appearing in a very thin sheath next to the cathode. Because the sheath is so thin, most of the discharge region is not effective in producing ozone.

If the ionization process is independent of electric field, the discharge can be uniform throughout the gap, and the chemical efficiency will be of the same order as that of the dc or low frequency units. However, the power density will be much greater (~50 W/cm^3) and the discharge gap can be considerably larger (e.g., 150 mm).

The projected operating characteristics of a radiofrequency electrochemical discharge are as follows:

<u>Unit Size</u>:	15 cm discharge gap
	30 cm wide
	120 cm long
<u>RF Power</u>:	
Power density	36 W/cm^3 (rms)
Frequency	20 MHz
Voltage (peak)	132,000 V
Total power	1.95 MW

O_2 Gas:

O_3 concentration (exit)	0.6%
Flow velocity	1670 ft/sec (M=1.6)
Static density	~0.33 ρ_o
Tons/day of O_3	10
Chemical efficiency	16% (assumed equal to 220 g/kWh, best efficiency in conventional ionizer)

Radiation Power:

Radiation input power to gap	3 kW (assumes n_e/n_{O_2} - ~10^{-2})

An ozone plant with a total production of 600 tons/day would require just 60 of the proposed ozonizers, and 113 MW(e) of electric power. The capital cost of the ozonizers, including power conversion equipment, would be on the order of $100/kW or ~10 million for the entire plant (not including contractors, O_2 preparation, and compressors).

The data on which these calculations were based are reasonably good. The principal uncertainty is the detachment rates of electrons from O^-, O_2^-, and whether O_3^- is important. If the electron detachment frequency is controlled by the vibrational temperature of O_2, and not the translational temperature, then the estimated detachment rates should be sufficient to make the process go. There is strong indication that this is so in microwave afterglow experiments with O_2.

We plan to make measurements of the attachment and detachment rates for electrons to form various negative ions in oxygen. This can be done conveniently with a Van de Graaff electron beam to provide the ionization in an experimental cell. Both dc and rf electric fields will be used, and the O_3 concentrations measured *in situ* spectrophotometrically.

1 Accession Number	2 Subject Field & Group	SELECTED WATER RESOURCES ABSTRACTS INPUT TRANSACTION FORM

5 Organization

Brookhaven National Laboratory
Upton, New York 11973

6 Title

Treatment of Acid Mine Drainage by Ozone Oxidation

10 Author(s)

M.Beller
C.Waide
M.Steinberg

16 Project Designation

Contract No. 14-12-838

21 Note

22 Citation

Environmental Protection Agency
Washington, D.C. 20242

14010FMH 12/70

23 Descriptors (Starred First)

Mine Drainage	neutralization	ferric iron
Iron Oxidation	limestone	treatment costs
Ozone	ferrous iron	

25 Identifiers (Starred First)

27 Abstract An engineering design and economic study to evaluate the feasibility of ozone oxidation and limestone neutralization of Acid Mine Drainage (AMD) was performed. The study concludes that an ozone process is feasibile, compares economically with existing processes, and offers potential advantages in process control, reduced neutralization costs, and simplified AMD sludge handling and disposal. Ozone production by electric discharge and radiation processes are compared both for on-site and central plant installations utilizing ozone shipping and storage facilities. A central chemonuclear ozone production plant with a distribution system is found to be most economical, followed by electric discharge central and onsite plants. Design and construction of a mobile pilot plant which employs electric discharge ozonizers is recommended for field trials of the process.

This report was prepared in fulfillment of Contract No.14-12-838 between the Federal Water Quality Administration and Brookhaven National Laboratory.

Key words: Mine drainage, ozone treatment, treatment costs, neutralization, limestone, oxidation, ferrous iron, ferric iron.

Abstractor	Institution
M. Steinberg	Brookhaven National Laboratory

WR:102 (REV JULY 1969)
WRSIC

SEND TO: WATER RESOURCES SCIENTIFIC INFORMATION CENTER
U.S. DEPARTMENT OF THE INTERIOR
WASHINGTON, D. C. 20240

* GPO: 1969-359-339